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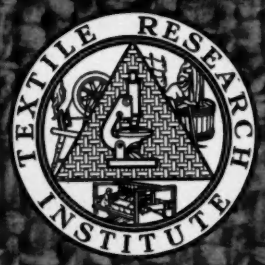

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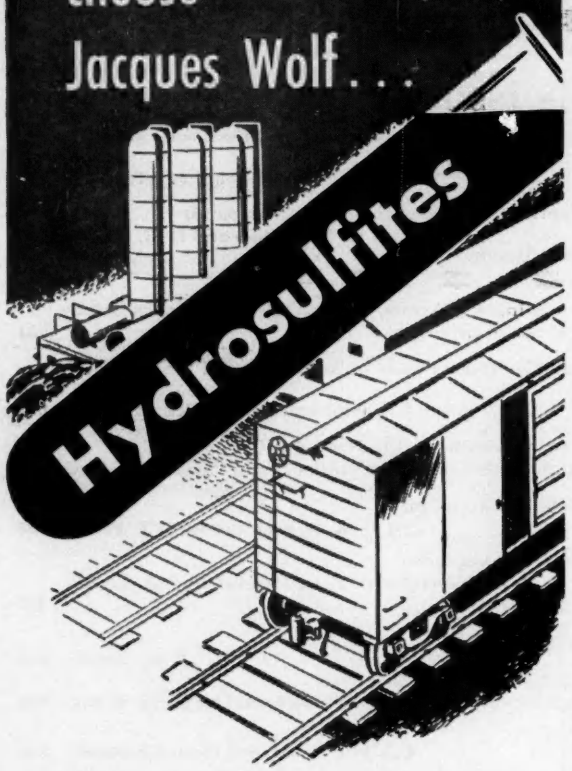

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TEXTILE RESEARCH JOURNAL

VOL. XXIV, No. 9 SEPTEMBER, 1954

The Application of Radiochemical Techniques to the Study of the Interaction of Hair Fibers with Aqueous Solutions

Paul B. Stam* and Howard J. White, Jr.†

Contribution of Textile Research Institute, Princeton, New Jersey, and Brookhaven National Laboratory, Upton, New York

Abstract

Radioactive tracer techniques have proved to be uniquely adaptable to the study of the interaction of hair fibers with various aqueous solutions including dye baths. NaBr solutions, NaBr-HBr solutions, NaCl solutions, and an acid dye bath containing a sulfur-labelled acid dye for wool were used.

It was found that appreciable amounts of NaBr were absorbed by hair from solution with a linear relationship existing between the equilibrium amount absorbed and the molarity of the treating solution. If acidic or basic solutions were used, additional absorption resulting from the well-known amphoteric properties of keratin was observed. In a preliminary experiment, the absorption of each of three components of an acid dye bath was followed by taking advantage of differences in radioactive behavior of the three species. Certain rate processes have also been followed.

Introduction

It is evident that a complete description of a complex process of partitioning such as dyeing requires a knowledge of the concentration of each component of the dye bath in the fiber under the dyeing conditions. To the best of our knowledge, complete information is not available on any single dyeing process and would be very difficult to obtain by conventional methods. For this reason we decided to investigate the possible utility of radioactive tracer techniques.

It soon became apparent that tracers were uniquely suited to studying some aspects of the dyeing process. The purpose of this paper is to show, to some extent, the versatility of tracer techniques in this application and to present some preliminary results on the interaction of fibers with aqueous ionic solutions. In particular, data will be given for the equilibrium uptake of sodium bromide by human hair from aqueous solutions at room temperature over an extended concentration range, for certain other equilibrium and rate experiments involving sodium bromide and sodium chloride, and for an experiment designed to simulate commercial practice, on the acid dyeing of hair. In all these experiments we consider that, qualitatively, hair will closely resemble wool in behavior.

Experimental

In essence, the radioactive tracer technique consisted in immersing a single hair in a solution containing a radioactively "tagged" salt. The fiber was then removed from the solution, washed, and its

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radioactivity measured. A comparison with the activity of a standard, consisting of a known amount of radioactive salt, gave the amount of salt taken up by the fiber.

Preparation of Hairs

Unmedullated blond human hairs, 10 cm. in length, were used. The hairs were from the same head as those used in swelling experiments previously reported [1]. They were solvent-extracted by the method used previously and washed in distilled water for several hours. No special buffering or dialyzing treatments were used. The pH of the distilled water was very nearly 6. The fibers were dried in a vacuum desiccator over magnesium perchlorate for at least 12 hrs., and then stored in the balance room.

An Ainsworth-type FDJ microbalance, with a sensitivity of 2.25 μ g./scale division, was used to weigh the fibers. The fiber weights fell in the range 150 μ g.–600 μ g., with the average weight about 300 μ g.

The balance room was kept at a contant temperature of 25.6 ± 1.0°C. The relative humidity had a seasonal range from 15% to 60%. However, the humidity was partially controlled by a Frigidaire Room Conditioner, and daily variations had a range of 5% or less. The conditioner acted to prevent any sudden changes in humidity.

The fibers were conditioned overnight in the balance room, and the humidity of the balance room was measured before and after each set of weighings with a sling psychrometer. The fibers were assumed to be at equilibrium at a humidity which was the average of the two humidity readings. Since the fibers were dried prior to conditioning in the balance room, they were considered to have approached equilibrium from the dry state and to be on the absorption side of the water absorption hysteresis cycle. The amount of water contained by each hair was determined from the average relative humidity and the absorption isotherm for hair taken by Chamberlain and Speakman [3]. By this procedure, the dry weight of each fiber was considered to be determined to within 1.5%

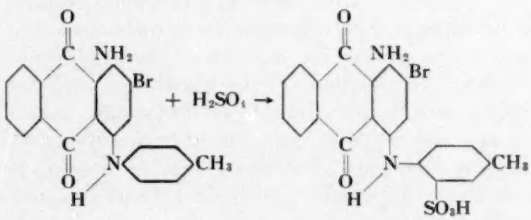
Preparation of Radioactive Solutions and Treatment of Fibers

Three radioactive isotopes were used, Na^{22}, Br^{82}, and S^{35}. The radioactive isotopes were obtained from Oak Ridge National Laboratory with permission of the U. S. Atomic Energy Commission.

The Br^{82} was obtained as crystalline KBr contaminated with radioactive K^{42}. A solution of the KBr was passed through an ion exchange column containing Amberlite IR100 or IR120 on the acid cycle. The resulting HBr was titrated with the appropriate alkali hydroxide, using a pH meter as indicator, and brought to the selected concentration and specific activity. The molar concentration scale was used.

The Na^{22} was obtained as NaCl in a weak HCl solution. The $Na^{22}Cl$ was passed through an ion exchange column on the acid cycle and eluted with acid containing the appropriate anion.

The S^{35} was incorporated into an acid dye for wool. The dye used was Anthraquinone Blue SKY (Color Index No. 1088), molecular weight 509. Its formula is given below. The synthesis of the radioactive dye was accomplished by sulfonation of the so-called dye base, which had been purified by recrystallization from ortho-dichlorobenzene, with radioactive sulfuric acid. The S^{35} was received as H_2SO_4 in 0.1*N* HCl (10 millicuries in 10 ml.). This solution was evaporated to one drop, and enough fuming sulfuric and 100% sulfuric acid were added to form 1.4 ml. of 100% sulfuric acid. Three grams of benzophenone were added, the temperature brought to 75°C, and the dye base added over a period of 1 hr. The dye acid formed was washed with ether and benzene and reprecipitated from 15% HCl, giving a radioassay of 700 counts/min./μg. The benzophenone serves as a diluent * to reduce the viscosity of the reaction mixture; in normal practice, a larger excess of H_2SO_4 would be used. The overall reaction is the following:



The dye was chosen because the sulfonation was simple and the formation of isomers unlikely.

Most of the data were taken at room temperature without temperature control. For higher temperatures, controlled temperature baths were used.

*We are indebted to Professor Gregg Dougherty of Frick Chemical Laboratory, Princeton University, for suggesting the use of benzophenone as a diluent.

The fibers were held at one end by a small stainless steel spring clamp which had a hook on the other end. The clamps were held by a wire loop in a test tube or a centrifuge tube, the solution was poured in over the fibers and the test tube was stoppered. The fibers were preswollen in moist air before being used. This was done to minimize the possibility of a rate-determining swelling process in rate-of-absorption experiments. Rate experiments were frequently made to determine the appropriate time of treatment necessary to obtain equilibrium data.

Removal from Solution and Washing Procedure

The clamps were removed from the solution, held with a pair of hemostatic forceps, and shaken vigorously to remove entrained droplets from the fibers. The fibers were then washed. The wash liquid used had the same composition and concentration as the treating liquid but did not contain any radioactive isotopes. Because of the wash liquid chosen little absorbed material was removed from within the fiber, and the washing process consisted of an exchange of radioactive ions on the surface of the fiber for inactive ions from the solution.

Figure 1 shows a plot of residual Na content of the fiber against log time in the wash liquid for the case of hair which had been brought to equilibrium with a 0.99*M* $Na^{22}Cl$ solution. Hairs which were not washed before counting showed a greater activity than any of the points on the curve. The initial flat portion of the curve in Figure 1 is taken to indicate that, in this time interval, the radioactive ions in droplets adhering to the surface of the hair have all been replaced by inactive ions from the wash solution but that no appreciable diffusion out from within the fiber has yet occurred. Washing times were chosen to fall within this interval.

Counting Equipment

All counting was done using a windowless flow counter operating in the proportional range. The counter, called a "Nucleometer," is a commercial instrument manufactured by Radiation Counter Laboratories, Skokie, Illinois.

Measurement of Activity of Solutions

One- or two-cc. samples of a conveniently dilute solution were evaporated on stainless steel discs to act as standards. The concentration of the solution was selected so that the average thickness of the standard deposit was less than 0.25 mg./cm.^{2} as measured by the amount of salt divided by the area covered. This thickness is such that self-absorption in the sample is negligible.

The chemical composition of each standard solution was determined by standard chemical analysis. In using Br^{82}, which has a 35-hour half life, all activity measurements were adjusted to a selected zero time to correct for radioactive decay. Usually 10,000 counts were measured for each sample.

Measurement of Activity of Fiber Samples

The fiber samples were coiled in a loose spiral of about 15-mm. diameter on stainless steel discs. A thin layer of albumen fixative on the disc was used to hold them in place. The fixative was denatured, and water was driven off from the sample by heating on a hot plate, after which the samples were ready to be counted. On some occasions tantalum discs were used, for reasons which will be discussed presently.

The basic step in the tracer method used is the comparison of radioactivity of the sample with that of the standard. Then, using the previously determined specific activity of the standard, the amount of salt taken up by the fiber can be determined. There is a difficulty, however, involving the measurement of the radioactivity. All of the radioactive decompositions in a given time are not measured by the counter, either in the case of the standard or of the sample. Furthermore, the fraction of the total number of decompositions per unit time measured is different for the sample and for the standard, so that it is necessary to multiply the activity measured for the fiber by a factor to convert it to an equivalent amount of standard solution. The reciprocal of this factor can be called the self-absorption factor for convenience. This practical self-absorption factor actually includes the effect of differences

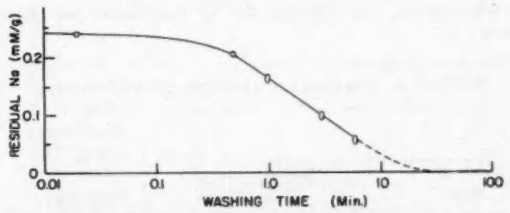


FIG. 1. *Desorption of active Na^+ from human hair when washed in inactive 0.99*M *NaCl.*

in absorption, scattering, and geometry between the mounted fibers and the standards.* The self-absorption correction factors used in obtaining the results given in this paper were determined experimentally by dissolving the mounted hairs with a volatile solvent and reprecipitating the protein material as a thin film. In the case of S^{35}, tantalum discs were used in determining the self-absorption correction, whereas the experiments reported herein were done using stainless steel discs. The error introduced in this way is thought to be small. Also the results in this paper have been increased by 8% to correlate them with results taken using a different washing technique. The alternative washing technique permits a wider variety of measurements to be made. Presumably the difference between the two wash methods involves differences in the amounts of salt absorbed on the fibers' surfaces. The details of the method of determining the self-absorption correction factor and the correlation between washing techniques will be discussed in a future paper.

In one experiment the amounts of three separate ions absorbed by one hair were measured. The measurement of the amounts of the individual ions by radiochemical means depended on the properties of the individual isotopes, which are given in Table I. The short half life of the Br^{82} makes it possible to estimate its activity in the presence of the activity of the other two isotopes by following the time rate of decay of the activity in the sample. Because of the lower maximum energy of the S^{35}, its radiation is absorbed to a greater extent in absorbers such as thin sheets of aluminum than is the radiation of the other two isotopes. The amount of absorption in a given absorber can be determined experimentally using samples of each pure isotope separately.

Thus, by combining data on the time rate of decay of activity from a sample containing all three isotopes with data on the decrease in measured activity caused by the introduction of aluminum foil absorbers between the sample and the counting volume, the activity resulting from each isotope can be measured.

* For a discussion of self-absorption, etc., see any text on radiochemistry—for example, that of Friedlander and Kennedy [6].

TABLE I. PROPERTIES OF RADIOACTIVE ISOTOPES

Isotope	Half life	Maximum energy of β radiation
Br^{82}	35 hrs.	0.465 Mev.
S^{35}	2,090 hrs.	0.167 Mev.
Na^{22}	22,800 hrs.	0.575 Mev.

Results and Discussion

Equilibrium Absorption Results

In Table II the results of several equilibrium absorption experiments are shown. These include uptake from NaBr solutions over an extended concentration range, uptake from one NaCl solution, and uptake of Na^+ from an acidic and a basic solution. The first column in Table II gives the composition of the treating solution, the second column, the tagged isotope, the third column, the concentration of the treating solution, and the last column, the amount of active isotope absorbed.

The neutral solutions used were prepared by titration of the appropriate acid or base. The solutions were kept stoppered and, although the pH was not measured consistently, it can be assumed to have remained close to pH 6 throughout the useful life of the solutions. For the experiments reported in Table II, it is unlikely that error resulting from acid or base absorption is appreciable. This is substantiated by the fairly good agreement between the results taken using Na^{22} and those taken using Br^{82}. If anything, a slight amount of base binding is suggested. Since the isoionic point of wool is at pH 6.2 [7], it is possible that, if some solutions had

TABLE II. EQUILIBRIUM UPTAKE OF Na^{22} AND Br^{82} FROM AQUEOUS SOLUTIONS AT ROOM TEMPERATURE

Solutes	Tagged isotope	Concentration of solution (M/L)	Uptake (mM/g.)
NaBr	Br^{82}	1.60	0.492
		3.20	0.983
		6.40	1.99
	Na^{22}	0.400	0.140
		1.05	0.380
		2.02	0.746
		3.13	1.13
		3.63	1.18
		5.01	1.49
		6.20	2.18
		6.36	2.20
		7.25	2.21
NaBr–HBr	Na^{22}	0.46 NaBr, pH 2.4	0.054
		0.44 NaBr, pH 11.2	0.296
	Br^{82}	0.025 NaBr, pH 1.9	0.573
NaCl	Na^{22}	0.99	0.234

acidities between pH 6.2 and 7.0, base absorption could occur. However, more extensive and precise measurements are needed to settle the point.

The results on the uptake from essentially neutral NaBr solutions show that appreciable amounts of this salt are taken up. The measurements made using NaBr-HBr solutions show the well-known amphoteric properties of keratin [8, 9], which form the basis for acid dyeing, in addition to the absorption of the salt. The results using a solution of pH 2.4 show that the uptake of salt, as represented by the Na^+ ion, is inhibited by the uptake of acid known to occur at that pH. The results taken at pH 11.2 show the absorption of base by the hair at this pH in addition to the absorption of salt. It is not possible to separate the amount of Na^+ absorbed into the part absorbed as base and the part absorbed as NaBr. A rough guess made using the results of Steinhardt and Harris [8] for KOH-KCl solutions suggests that more than 0.2 mM/g. of base should be absorbed at this pH. If this is true the absorption of salt must also be inhibited by the absorption of base. In the next entry in Table II, the uptake of Br from an acid solution is shown. Undoubtedly most of the Br is absorbed as HBr. The uptake is much too high for the Br to be in the form NaBr, but of the right order of magnitude for it to be HBr, if the work of Steinhardt and Harris [8] on HCl-KCl solutions is used as a comparison. The last line of Table II gives results on the amount of NaCl absorbed by hair which show that NaCl is analogous to NaBr although absorbed to a lesser extent at the concentration used.

In Figure 2 the amount of salt taken up from NaBr solutions by hair is plotted as a function of the concentration of the solution. The points fall rather closely around a straight line through the origin, and it is interesting to speculate as to the significance of this linear relationship.

In the first place, if the fiber is considered to constitute a capillary system of fixed volume it is obvious that such a linear relationship would exist, providing no selective absorption of one component on the walls of the capillaries occurred. This is a tempting hypothesis in view of the lack of any known absorption sites for either Na^+ or Br^- in the fiber. However, it has been shown [1] that swelling of hairs occurs in NaBr solutions so that caution is necessary in adopting any mechanism requiring an essentially constant volume. Although the increase in swelling is only 4% compared to the volume of the hairs in liquid water, this is roughly a 17% increase in the capillary volume within the fiber, and such a change in capillary volume could not be ignored.

Other possible explanations of the salt uptake and swelling results would involve the specific absorption of one or both of the ions absorbed. While the linear relationship shown in Figure 2 does not have any special significance in terms of such mechanisms, it does not contradict them. The swelling behavior, on the other hand, can be more readily understood in terms of a specific absorption. Other measurements are necessary to determine which possible mechanism most nearly approximates the experimental results over a range of behavior.

Rate of Absorption

Measurements on the rate of absorption have been taken primarily to determine the length of time necessary to ensure the attainment of equilibrium. However, certain general features of the rate measurements are of interest.

In the first place the ratio of amount of fiber to amount of solution is such that the solutions do not change in concentration during the experiments. As has been mentioned the fibers were preswollen in water vapor in an effort to minimize possible rate-controlling swelling effects. It has been shown by swelling measurements [1] that, for hair in more concentrated solutions, swelling changes which may be rate controlling cannot be avoided in this way. However, for dilute solutions, such as were used in the rate work reported here, swelling changes should

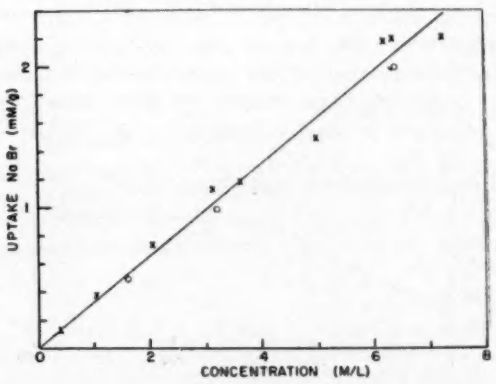


FIG. 2. *Equilibrium absorption of NaBr by human hair at room temperature as a function of molarity of NaBr.*

not be important. Of possibly greater importance is the fact that no uniform stirring was used; the tubes holding the solutions were, at most, swirled only occasionally. Since penetration of a mass of fibers was not necessary, there is no direct connection between the well-known need for stirring in bulk-dyeing experiments and the possible need in single-fiber experiments. Although it seems unlikely to us that transport through the aqueous phase can be rate controlling in the case of single fibers, the possibility remains open at the present time. One final source of possible error must also be noted. The self-absorption correction factor was obtained using fibers which had been brought to equilibrium and which were presumably uniformly permeated with salt. A nonuniform distribution of the salt throughout the fiber could change the effective self-absorption coefficient and introduce error into the initial points in a rate experiment. The magnitude of the error resulting from this effect is again presumed to be small and remains to be determined but is certainly less than the self-absorption correction.

Two rate-of-absorption measurements are shown in Figures 3 and 4. The points were taken using different fibers, each point being the average for two or more hairs. The fibers were selected to be as nearly the same in diameter as possible to minimize effects of fiber size. Figure 3 shows the rate of absorption of Na^{22} from a 0.99*M* solution of NaCl, and Figure 4 shows the rate of absorption of Br^{82} from a solution 0.035M in Br and 0.025*M* in Na, having a pH 1.92. The solid lines in each figure represent attempts to apply Fick's Law to the results. The equation used was derived under the assumptions that the diffusion constant is independent of concentration within the fiber and that the diameter of the fiber remains constant, and describes radial diffusion into a cylindrical fiber initially free of diffusant from a solution of constant concentration [2]. It can be written:

$$\frac{Q}{Q_\infty} = 1 - \frac{4}{a^2} \sum \frac{1}{\alpha_n^2} \epsilon^{-\alpha_n^2 Dt},$$

where Q is the amount absorbed at time t; Q_∞, the amount absorbed at equilibrium; D, the diffusion constant; a, the radius of the fiber, taken to be 30 μ; and where the α_n involve constants and a.

In Figure 3 the diffusion of NaCl into hair is shown. The experimental points do not fall on the Fick's Law plot. The diffusion constant of the Fick's Law plot is 3.2×10^{-9} cm.²/sec., showing that the diffusion process is decidedly slower than an aqueous diffusion process ($D = 10^{-5}$ to 10^{-6} cm.²/sec.).

The diffusion process followed in Figure 4 is probably the diffusion of HBr into the fiber. The points more nearly fall along the theoretical curve which has a smaller diffusion constant, $D = 5.4 \times 10^{-10}$ cm.²/sec.

It is well known that diffusion processes in high polymeric materials often do not obey Fick's Law, and some further analysis of the reasons for deviations has been given by Crank [4]. However, in view of the rather sketchy nature of the results given, it would be premature to speculate on the reasons for the deviation from Fick's Law shown in Figure 3 and the differences between Figures 3 and 4.

Absorption of Thre Components from a Dye Bath

The measurement of the uptake of each of three components from a dye bath was accomplished in the following way. The dye was an acid dye for wool containing a sulfonic acid group. The method of incorporating radioactive sulfur into this dye has

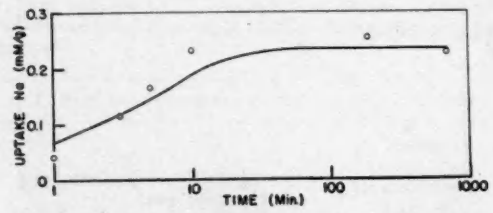


FIG. 3. *Rate of absorption of Na^+ by human hair from 0.99M NaCl solution. The line represents an application of Fick's Law.*

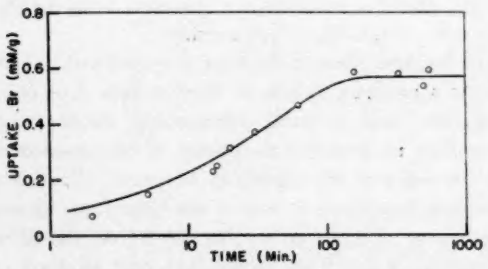


FIG. 4. *Rate of absorption of Br^- by human hair from NaBr-HBr solution (pH 1.92, [Na^+] 0.025M, [Br^-] 0.035M). The line represents an application of Fick's Law.*

TABLE III. UPTAKE OF IONS FROM AN ACID DYE BATH BY HAIR

Time in solution			
2 hrs.		20 hrs.	
Substance	Uptake mM/g.	Substance	Uptake mM/g.
Dye	0.19	Dye	0.59
Br^-	.51	Br^-	.10
Na^+	—	Na^+	.24

been outlined in the experimental section. NaBr and HBr w[illegible] used to produce the desired ionic strength and acidity, and Na^{22} and Br^{82} were used as tracers for the Na and Br ions. Thus three of the four ionic constituents of the dye bath were tagged, each with a different isotope. The method of determining the amount of radiation from each isotope has also been outlined in the experimental section.

The composition of the dye bath was the following: Dye, 0.037 g./L Anthraquinone Blue SKY; Na^+, 0.02 M/L; H^+, 0.01 M/L; Br^-, 0.03 M/L. The temperature of the bath was kept at 94.5°C. An inactive dye bath of the same composition was used as a wash liquid. Samples were removed from the bath after 2 hrs. and 20 hrs. Microscopic examination of cross sections of the hairs dyed 20 hrs. showed a visually uniform dyeing, indicating that equilibrium had been reached or nearly reached.

The results are shown in Table III. Since results on only two hairs are shown in Table III, the values have qualitative significance only. They are presented as indicative of a type of experiment which can be run using tracers and because they show certain gross features of the acid dyeing process. Two features of Table III can be pointed out. First, the concentration of the bromide ion within the fiber reaches a maximum in time. Apparently the slower moving but more tenaciously held dye ion can replace it within the fiber and ultimately cause it to be expelled from the fiber. This is in agreement with the work of Elöd [5]. Second, although the sodium ion is present in greater concentration than the hydrogen ion in the dye bath, the hydrogen ion is present in excess in the fiber. The hydrogen ion in the fiber is determined by using the principle that the fiber is electrically neutral. Again the excess hydrogen ion absorbed is to be expected from the known affinity of keratin for hydrogen ions.

Acknowledgment

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A Study of the Weathering Characteristics of Cotton Fabrics Containing Inorganic Compounds*

Part I: Chromic Oxide and Copper in Inorganic and Organic Forms

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Abstract

A study has been made of the effect of outdoor weathering on unbleached and bleached cotton duck treated with (*a*) oxides of chromium and iron and copper carbonate, singly and in mixtures, (*b*) oxides of chromium and iron aftertreated with copper-containing organic fungicides —*viz.*, copper naphthenate, copper 8-hydroxyquinolinolate, and the copper salt of dehydroabietyl amine—and (*c*) chromic oxide, copper 8-hydroxyquinolinolate, and mixtures of these. A limited amount of data has been obtained with the above-mentioned inorganic treatments on lightweight cellulosic fabrics.

The data have confirmed previous observations to the effect that the presence of chromium and copper, in inorganic form, confers marked protection against actinic breakdown of the cellulose and also prevents the severe loss of copper which, in the absence of chromium, occurs during weathering. These effects were also noted, in lesser degree, with chromium-treated fabrics aftertreated with copper-containing organic fungicides. The lightweight fabrics treated with inorganic chromium-copper showed resistance to actinic degradation, but underwent severe loss of copper.

Introduction

The efficacy of various finishing treatments, applied to cotton fabrics for the purpose of imparting resistance to the effects of outdoor exposure, has been the subject of numerous investigations in recent years. While this work has related mostly to the needs of the Armed Services, it must not be forgotten that the problem is one which has an important bearing in the general consumer field, in which there is a very large annual waste of fabrics, chiefly cotton, as a result of exposure outdoors to the complex circumstances of deterioration usually referred to as "weathering."

The term "weathering" may be defined somewhat more precisely in terms of the various deteriorating influences involved [1]—*e.g.*, actinic, microbiological, etc.— but there is relatively little published information on the extent to which interplay of these influences is of importance with regard to the overall result.

The part of the weathering process which relates to microbiological deterioration has received considerable study as the result of conditions which arise when cotton fabrics are used outdoors under tropical or subtropical conditions. On the other hand, actinic degradation has probably received less attention than its importance warrants; for it is obvious that, while not all cotton fabrics used outdoors are necessarily subjected to the action of microorganisms, all of them are subjected to the action of sunlight. However, it is desirable to give both of these factors due consideration, and to attempt to design treatments which will ameliorate both of these effects.

So far, it has not been possible to obtain a durable treatment which will reduce actinic degradation and also give a high degree of protection against microbiological attack. This is primarily due to the fact that, in weathering, the most effective fungicides are removed with comparative ease from the treated fabric, presumably as a result of their water-solubility or, in the case of organic fungicides, of the water-solubility of the products formed by their breakdown on the fabric. Thus, for example, copper in the form of copper carbonate or cuprammonium, unless present in amounts greater than 0.5%, is lost rapidly under conditions of weathering involving moderate rainfall, the same being true of organic copper compounds such as copper naph-

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thenate and copper 8-hydroxyquinolinolate; and, indeed, it has been this laboratory's experience that all of the organic fungicides so far examined are removed from cotton fabric at a relatively rapid rate unless they are applied in conjunction with protectants such as waxes or other hydrophobic materials. While waxing treatments are frequently desirable to impart water-resistance to the treated fabrics, they may, for some uses, impart undesirable properties such as impairment of air porosity and stiffening at low temperatures. Moreover, data obtained in these laboratories, to be published shortly, show that certain types of petroleum-base waxes can lead to increased actinic breakdown of cellulosic fabrics.

Of the inorganic treatments in general use, chromium oxide, applied to the fabric by the precipitation by alkali of a soluble chromic salt, is known to give a considerable measure of protection and is extremely stable to weathering, but confers only a minor resistance to microbiological attack.

A summary of the literature in this field up to the end of 1946 has been given elsewhere [15]. Since that time, the results of a few investigations relating to weathering have been published, and in some cases these have included a study of the protective effects of certain inorganic treatments.

Race [12], in a paper dealing with the degradation of cotton during atmospheric exposure in industrial regions, referred to the protective action of chromic oxide, first noted by Cunliffe and Farrow [6], and gave two possible explanations of this—*viz.*, (*a*) it is a purely physical action, in which the chromic oxide absorbs radiation in the wave length slightly below 3,500 Å., which is known to cause photochemical tendering of cellulose; (*b*) the action is due to the formation of covalent linkages with the hydroxyl groups of the cellulose. It was admitted, however, that neither of these possibilities had been fully explored.

Block [4] studied, over a 2-year period, the weathering characteristics of a number of fungicides applied to 10-oz. cotton duck which had been extracted with hot ethyl alcohol to remove some of the noncellulosic constituents. The effects of the weathering were assessed by measuring loss in breaking strength and residual fungicide. In addition to the weathering tests, the resistance to microbiological attack of the samples was determined by the soil-burial procedure, the results of this test showing, in general, good correlation with those of the outdoor exposure tests. Of the treatments containing copper, the chromate was found to give excellent protection over the 2-year period.

Dean and coworkers [8] reported on the relative efficacies of various copper compounds in preventing microbiological deterioration of cotton burlap sandbags, and also on the breakdown in weathering of untreated cotton duck [9]; they also compared the relative stability to weathering of bleached and unbleached cotton duck [7].

Work carried out by the American Association of Textile Chemists and Colorists [13] on the weathering characteristics of cotton duck treated with various pigments, with and without synthetic resin finishes, showed that certain pigments—notably lead chromate, chromic oxide, and antimony oxide—gave considerable protection.

The data reported in this paper are an outcome of previous work designed primarily to study the effectiveness, as fungicides, of certain inorganic treatments. The earlier work had given indications that mixtures of certain inorganic compounds—notably, of chromium oxide and copper carbonate—reduce actinic degradation in cotton. Moreover, in such treatments the loss of copper on weathering was considerably less than when this metal was present alone, and, for this reason, the fungicidal efficacy of the treatment was superior to that of a copper treatment alone. The present work has confirmed the accuracy of the earlier observations, and includes a more detailed study of the limiting amounts of compounds required. The work has as its primary object the study of the ability of these treatments to protect cotton from actinic breakdown. But there has also been included in the study the assessment of the fungicidal efficiency of the various treatments, before and after weathering, as measured by the soil-burial technique.

Materials and Treatments

The fabrics used were as follows:

Unbleached duck.—An unsized army duck weighing 11.7 oz./sq.yd. (10 oz. commercial designation), and having 53 3-ply warp and 43 3-ply weft yarns/inch.

Bleached duck.—A portion of the unbleached duck which had received commercial scour and full bleach. The weight was 10.8 oz./sq.yd., and the number of warp and weft yarns per inch were 58 and 39, respectively.

Mineral-dyed duck.—A portion of the unbleached duck which had received commercial mineral-dyeing treatment. It had a weight of 10.6 oz./sq.yd., and 55 warp and 38 weft yarns/inch. The contents of chromic oxide (Cr_2O_3) and of ferric oxide (Fe_2O_3) were 0.21% and 1.22%, respectively.

Cotton nainsook.—A fully bleached fabric weighing 2.7 oz./sq.yd., woven from singles yarns, and having 100 warp and 100 weft yarns/inch.

Saponified acetate rayon.—A fully bleached fabric weighing 2.0 oz./sq.yd., woven from singles yarns, and having 88 warp and 88 weft yarns/inch.

With the exception of the commercial mineral dyeing treatment referred to above, all treatments were carried out in the laboratory.

The inorganic treatments were applied by a two-bath method to 6 in. × 18 in. specimens, selected at random from the piece, which had been previously wetted out in a 0.05% solution of commercial dioctyl sodium sulfosuccinate. In carrying out the treatments, the wetted-out specimens were immersed in a beaker containing a solution of requisite strength of the inorganic salt, removed quickly, passed through rubber-covered squeeze rolls, and again immersed in the solution, the process being repeated twenty times over a period of 15 min. at a bath temperature of 70°C. The specimens were then immersed in the second bath, which consisted of a 5% solution of sodium carbonate, passed through the rolls, and again put in the bath, the whole process being repeated seventeen times over a period of 10 min. at a bath temperature of 50°C. The specimens were then rinsed for 2 hrs. in running tap water at room temperature. Analysis of specimens showed that good uniformity of treatment was obtained by the above procedure. For analysis for the oxide content of a given treatment, a 6 in. × 1 in. warpwise strip was removed from each treated specimen and cut into pieces approximately ¼ in. square; these were mixed well and sampled.

In carrying out the organic aftertreatments, the copper naphthenate was applied from solution in Stoddard solvent, the specimens being immersed in the solution and given one pass through the rolls, with three thicknesses of blotting paper on each side of the specimens. The copper 8-hydroxyquinolinolate was applied in two different ways—*viz.*, from a solvent solution of the "solubilized" material, as above, and from an aqueous emulsion of the compound, diluted with water to the appropriate strength. In the latter case the specimens were wetted out as above, immersed in the dispersion, and passed through the rolls, the process being repeated until the required pickup was obtained (2–3 times).

The treatments with the copper salt of dehydroabietyl amine were from solution in Stoddard solvent or from an aqueous dispersion of the compound, and were carried out similarly.

All chemicals used in the treatments were of technical grade.

Test Methods

The following are the details of the methods used to determine the metal contents of the treated fabrics:

Chromium.—A 3–5 g. sample, accurately weighed, was ashed at 600°C in a porcelain dish, and the residue was dissolved in concentrated nitric acid with a few grams of potassium chlorate added. The mixture was evaporated to dryness, taken up in hydrochloric acid and again evaporated to dryness, again dissolved in hydrochloric acid, and sodium peroxide added until alkaline. The mixture was heated to boiling and filtered through a No. 1 Whatman paper to remove any ferric hydroxide present, and the filter was washed with hot water. The filtrate, containing the chromium as chomate, was made nearly acid with sulfuric acid, and boiled with 5–6 g. potassium acid sulfate to decompose excess peroxide. It was then acidified with sulfuric acid, 5 ml. of the acid per 100 ml. solution added in excess, and cooled. Two grams of potassium iodide were added, and the liberated iodine was titrated with 0.1*N* thiosulfate with starch indicator (1 ml. 0.1*N* thiosulfate = 0.001734 g. chromium).

Iron.—The procedure was as above except that the precipitate of ferric hydroxide, after washing, was dissolved in hot dilute hydrochloric acid, and a 6% solution of stannous chloride was cautiously added until the color disappeared. The mixture was cooled, 10 ml. of saturated mercuric chloride was added, and then 15 ml. of Knop's solution (150 ml. concentrated sulfuric acid and 150 ml. phosphoric acid diluted to 1 liter) and 3 drops of diphenylamine indicator were added, followed by titration with 0.1*N* potassium dichromate solution to a violet-blue color (1 ml. 0.1*N* dichromate = 0.0056 g. iron).

Copper.—An accurately weighed sample of approximately 1 g. was ashed at 600°C; the residue was dissolved in concentrated nitric acid, diluted with water, and made ammoniacal to precipitate any

iron present. The mixture was filtered and made up to a known volume, and suitable aliquots were taken. Where copper was present on the sample in an amount of 1% or greater, it was determined electrolytically. When present in smaller amounts, it was determined colorimetrically, using the color developed with sodium diethyldithiocarbamate as read on a Beckman DU Spectrophotometer. To do this, an aliquot containing 0.05 to 0.15 mg. copper was transferred to a 100-ml. volumetric flask and diluted to about 70 ml. with copper-free distilled water 3 ml. of concentrated ammonium hydroxide and 5 ml. of 1% gum arabic solution added to stabilize the developed color, followed by 10 ml. of a 0.1% solution of sodium diethyldithiocarbamate and making up to volume with water. The intensity of the color of the solution compared with that of suitable standards was read at 450 mμ.

The breaking strengths reported herein are the averages of 10 replicate measurements carried out on 1-in. wide ravelled warpwise strips broken on a pendulum-type machine operating at a pulling clamp speed of 12 in./min., the distance between clamps at the beginning of the test being 3 in.

The methods used for leaching, soil-burial, and cuprammonium fluidity were those used previously [15].

Data

Of the weathering exposures covered in this work, those of the inorganic treatments on the cotton duck and the organic aftertreatments on the mineral-dyed duck were carried out for a period of 4 months, from June 13 to Oct. 14, 1952; those on the cotton nainsook and regenerated cellulose rayon and the copper 8-hydroxyquinolinolate treatments on the unbleached duck containing a range of concentrations of chromium oxide were carried out for a similar period from June 12 to Oct. 13, 1953. Data for rainfall and hours of sunshine during the exposure periods are given in Table I. It will be noted that, with the exception of the rainfall, which was somewhat less during the exposure of the 1953 series, the weather conditions were very similar.

1. Experiments with 10-oz. Cotton Duck

(a) Cotton duck treated with mixtures of inorganic compounds.—The data are given in Table II. The work comprised a series of experiments designed to

TABLE I. WEATHER CONDITIONS DURING EXPOSURE OF SAMPLES

1952					1953				
Period	Mean daily temp. (°F) Max.	Min.	Rainfall (in.)	Bright sunshine (total hrs.)	Period	Mean daily temp. (°F) Max.	Min.	Rainfall (in.)	Bright sunshine (total hrs.)
June 13–June 14	81	49	0	26	June 12–June 13	73	46	0	20
June 15–June 21	76	53	0.09	84	June 14–June 20	80	56	0.42	65
June 22–June 28	79	57	1.91	53	June 21–June 27	79	58	0.52	76
June 29–July 5	81	58	0.30	80	June 28–July 4	79	58	0.47	58
July 5–July 12	82	60	2.94	62	July 5–July 11	74	54	0.83	59
July 13–July 19	86	64	0.11	57	July 12–July 18	86	60	0	60
July 20–July 26	82	61	0.72	57	July 19–July 25	81	62	0.57	51
July 27–Aug. 2	77	53	0.53	75	July 26–Aug. 1	79	60	0.34	66
Aug. 3–Aug. 9	77	55	1.28	60	Aug. 2–Aug. 8	74	54	1.53	54
Aug. 10–Aug. 16	78	60	2.49	55	Aug. 9–Aug. 15	78	60	0.90	64
Aug. 17–Aug. 23	73	53	1.12	66	Aug. 16–Aug. 22	72	47	0.25	76
Aug. 24–Aug. 30	82	55	0	75	Aug. 23–Aug. 29	88	63	0.07	58
Aug. 31–Sept. 6	75	57	0.62	30	Aug. 30–Sept. 5	89	63	0.95	49
Sept. 7–Sept. 13	77	52	0.27	49	Sept. 6–Sept. 12	72	47	0.45	51
Sept. 14–Sept. 20	67	51	1.18	22	Sept. 13–Sept. 19	60	43	1.71	19
Sept. 21–Sept. 27	62	41	0.37	42	Sept. 20–Sept. 26	63	46	1.09	44
Sept. 28–Oct. 4	66	41	0.70	37	Sept. 27–Oct. 3	69	43	0.41	55
Oct. 5–Oct. 11	51	33	0.46	23	Oct. 4–Oct. 10	53	39	0.64	22
Oct. 12–Oct. 14	63	35	0	13	Oct. 11–Oct. 13	48	33	0.07	8
Average	74	52	15.09	966	Average	74	53	11.22	955

examine the weathering characteristics of unbleached duck treated with various percentages of chromic oxide, with ferric oxide in the amount approximating that usually employed in the mineral-dyeing process (around 1%), mixtures of this percentage of ferric oxide and various percentages of chromic oxide, various percentages of copper carbonate (given as the oxide) up to what may be regarded as a practical limit, and, finally, a series containing mixtures of copper carbonate and chromium oxide designed to give information on the optimum mixture with respect to breaking strength loss and loss of copper on weathering.

It was also of interest to determine whether the removal of the noncellulosic constituents of the unbleached duck affected the behavior of these treatments, and, hence, a few experiments with fully-bleached duck have also been included.

It will be seen that with unbleached duck, a chromic oxide content of as little as 0.14% gave a markedly lower breaking strength loss on weathering than was the case with the untreated control, this protection being increased still further at an oxide content of 1%, where the breaking strength loss was 29%, which is in good agreement with the value of 26% found in the earlier work [15]. None of these treatments provided any protection against the effects of soil-burial.

The protection given by ferric oxide alone (0.85%) was of the same order as that given by the highest content of chromic oxide.

TABLE II

Treatment			Breaking strength loss (%)				
CuO (%)	Fe_2O_3 (%)	Cr_2O_3 (%)	Weathered	Leached and buried 2 wks.	Leached and buried 4 wks.	ΔF on weathering (rhes)	Loss of copper (%)
			10-oz. Unbleached Duck				
	none		51	100	—	14.2	—
—	—	0.14	39	100	—	12.6	—
—	—	0.53	36	100	—	13.0	—
—	—	1.03	29	100	—	13.6	—
—	0.85	—	31	100	—	12.7	—
—	0.97	0.10	24	100	—	10.1	—
—	0.94	0.63	18	93	—	5.6	—
—	0.70	0.98	18	89	—	7.0	—
0.23	—	—	37	27	62	15.1	94
0.58	—	—	40	18	30	17.0	96
1.05	—	—	45	6	4	18.6	96
0.20	—	0.16	25	95	91	8.0	66
0.11	—	0.76	16	97	100	6.3	51
0.09	—	1.16	16	96	100	7.2	26
0.66	—	0.14	31	7	2	10.1	82
0.69	—	0.86	13	47	59	5.7	49
0.61	—	1.29	10	68	51	5.4	31
1.30	—	0.10	37	2	0	12.2	86
1.16	—	0.78	11	9	3	5.9	53
1.21	—	1.45	11	13	36	5.2	36
			10-oz. Bleached Duck				
	none		41	100	—	16.4	—
—	—	0.64	28	100	—	12.9	—
0.36	—	—	41	18	35	20.7	99
0.59	—	0.69	13	—	34	8.5	84
0.55	—	1.16	13	—	77	8.1	78

The samples treated with the mixtures of chromic and ferric oxides showed considerably lower breaking strength losses and fluidity increases than those obtained when the oxides were used separately. It would seem that a mixture of chromic oxide at a concentration of 0.6% or higher and ferric oxide at a concentration of approximately 1% gives the maximum protection. It is also of interest to note that such mixtures offered some slight protection against deterioration in soil-burial.

When used alone, copper carbonate appeared to afford some slight protection to the fabric, as judged by the breaking strength loss. As the concentration increased, the extent of deterioration also increased, as shown by both breaking strength loss and fluidity data. The loss of copper on weathering was almost complete in all cases.

The series of treatments containing both copper and chromium falls into three groups. The copper was present as carbonate, but for purposes of comparison is expressed as the oxide. The first group consists of copper carbonate at a concentration of 0.1%–0.2% (oxide) used with chromic oxide at concentrations of approximately 0.15%, 0.75%, and 1.2%, the second of copper carbonate at a concentration of approximately 0.6% (oxide) used with chromic oxide at the above concentrations, and the third of copper carbonate at a concentration of 1.15%–1.30% (oxide) again used with chromic oxide at the same range of concentrations. It may be seen that in all cases there was considerable protection against the effects of weathering, the most effective treatments being copper carbonate at concentrations of 0.6% and 1.2% with chromic oxide of the same concentrations. In general, protection against the effects of soil-burial increased with increase in copper content. The effect of these mixed copper and chromium treatments in reducing the loss of copper in weathering is striking, the loss in any mixture containing 1% chromium oxide being reduced to approximately one-third of that shown by the samples containing copper carbonate alone. These treatments also showed marked trends with respect to the breaking strength losses shown by the weathered samples and by the resistance to soil-burial. In the samples containing the lowest content of chromic oxide, there was a progressive increase in the breaking strength losses on weathering with increase of copper carbonate content. With increasing content of chromic oxide, these losses were sharply reduced. The fluidity data, in general, show a similar trend. As would be expected, resistance to soil-burial was greatest in the samples containing the highest contents of copper. In Table III the data for chromic oxide and copper carbonate when used alone and in mixtures are further compared on the basis of low, medium, and high contents of oxides.

The results of the chromium-copper series confirm the previous observation [15] made on a sample similarly treated containing approximately 1.0% each of chromium and copper, expressed as oxides, which showed no significant loss of strength after a similar weathering period or when subjected to soil-burial.

The unique effect of mixtures of chromium and copper compounds in affording protection does not appear to have been noted by previous workers. Thus, for example, Jarrell and coworkers [13], who studied the weathering characteristics of cotton duck treated with chromium, iron, and copper, separately and in mixtures, concluded that the fungicidal effect

TABLE III. COMPARISON OF PROTECTIVE EFFECTS OF CHROMIUM AND COPPER USED SEPARATELY AND IN MIXTURES

Level of oxide content		Breaking strength loss (%)			Increase in cuprammonium fluidity (rhes)		
		Oxides used separately		Oxides used together	Oxides used separately		Oxides used together
CuO	Cr_2O_3	CuO	Cr_2O_3		CuO	Cr_2O_3	
low	low	37	39	25	15.1	12.6	8.0
low	medium	37	36	16	15.1	13.0	6.3
low	high	37	29	16	15.1	13.6	7.2
medium	low	40	39	31	17.0	12.6	10.1
medium	medium	40	36	13	17.0	13.0	5.7
medium	high	40	29	10	17.0	13.6	5.4
high	low	45	39	37	18.6	12.6	12.2
high	medium	45	36	11	18.6	13.0	5.9
high	high	45	29	11	18.6	13.6	5.2

of copper was about the same when used alone as when used in mixture with the other compounds. In a study of the effectiveness of chromic oxide, ferric oxide, and copper carbonate, separately and together, Race [11] found that mixtures of chromic oxide and copper carbonate did not substantially improve the fastness to laboratory washing in water at pH 5.3 to 5.5; but it was found that the incorporation of ferric oxide did markedly reduce the loss of copper. It should be pointed out that Race's studies were directed to weathering effects occurring in industrial atmospheres known to impart appreciable acidity to the rain that falls through them, and, hence, his results are not strictly comparable to those of the present experiments, in which the weathering was carried out in a nonacidic atmosphere.

The only other data on the use of copper and chromium together are those of Block [4], who found that 0.5% copper chromate, deposited on the cloth by double decomposition of cupric acetate and sodium chromate in a two-bath treatment, gave excellent protection to unbleached cotton duck exposed to weathering in Florida. He reported a breaking strength loss of 16% in one year's weathering and good resistance to soil-burial (34% loss in strength in 2 weeks). The loss of copper in weathering was approximately 86% in one year's weathering under conditions of considerably greater severity than those of the present study.

There is some indication, from the present work, that a ratio of chromic oxide to cupric oxide of 1 : 1 gives the highest degree of protection. Thus, if the data for the copper-chromium series are plotted (see Figure 1) in the form of breaking strength loss *vs.* molar ratio Cr_2O_3/CuO for the low (0.1%), medium (0.75%), and high (1%) copper oxide contents, the breaking strength losses appear to become constant at the point representing the maximum content of chromic and copper oxides in equimolar quantities. The curve for the high copper oxide experiments cannot be drawn with any degree of certainty owing to the low ratios of Cr_2O_3 to CuO employed. This effect is being studied further.

If a 1 : 1 ratio of Cr_2O_3 to CuO is found to give maximum protection, this would suggest that a compound having the composition of copper chromite may be involved, although the published information on this compound does not indicate that it would be formed readily under the conditions of the experiments reported here.

The data from the limited series of experiments with bleached duck are given in Table II. It may be seen that the breaking strength loss of the untreated bleached fabric is somewhat less than that of the unbleached duck. The difference, though small is significant, and may be due largely to differences in minor amount of microbiological attack during weathering, since it has been shown by Fargher [10] that the presence in unbleached fabrics of small amounts of nitrogenous and other materials tends to encourage the growth of microorganisms on such fabrics. About 0.5% chromic oxide on the fabric gave about the same degree of protection as with the unbleached fabric. Treatment with copper carbonate alone afforded no protection against weathering, but the effects of the chromic oxide-copper carbonate treatments were similar to those on the unbleached duck. The increase in fluidity of samples containing copper was somewhat higher than with the unbleached duck, although this was not reflected in higher breaking strength losses. There was a marked difference in the extent to which the copper was retained, on weathering, by the two types of duck, the losses in the case of the bleached duck being very large, amounting to 78% in the sample containing 0.55% copper oxide plus 1.16% chromic oxide. Reference is made later in this paper to the significance of this observation.

(*b*) *Mineral-dyed duck aftertreated with organic fungicides containing copper.*—These experiments were an extension of earlier work [2] which had shown that when copper naphthenate is subjected to water-leaching or weathering, it undergoes an appre-

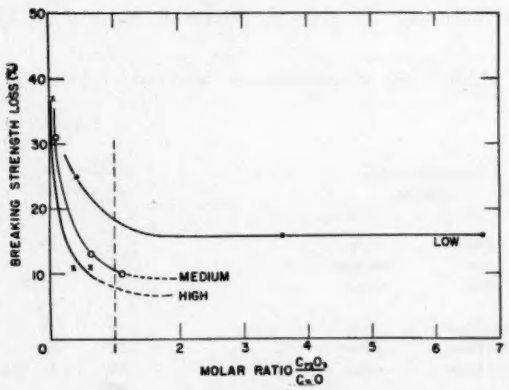

FIG. 1. *Effect of the ratio of Cr_2O_3 to CuO on the breaking strength loss of unbleached cotton duck exposed to weathering.*

TABLE IV. PROTECTIVE EFFECTS OF MINERAL-DYED DUCK AFTERTREATED WITH ORGANIC FUNGICIDES CONTAINING COPPER

Copper aftertreatment	Original copper on fabric (%)	Breaking strength loss (%) Weathered	Leached and buried 2 wks.	Leached and buried 4 wks.	ΔF on weathering (rhes)	Loss of copper (%)
none	—	28	88	—	10.0	—
Copper naphthenate (applied from solvent)	0.09	35	80	93	11.0	74
	0.25	34	38	51	12.1	69
	0.52	34	0	10	16.4	63
Copper 8-hydroxyquinolinolate (solubilized, applied from solvent)	0.03	29	2	0	8.4	64
	0.06	27	0	0	8.0	68
	0.15	26	0	0	6.7	80
Copper 8-hydroxyquinolinolate (applied from water dispersion)	0.04	25	0	12	9.9	47
	0.09	24	0	0	9.9	61
Copper salt of dehydroabietyl amine (applied from solvent)	0.07	31	3	3	8.4	60
	0.27	25	9	0	8.5	70
Copper salt of dehydroabietyl amine (applied from water dispersion)	0.13	21	0	0	8.6	78
	0.17	27	2	0	9.3	77

ciable amount of hydrolysis, a portion of the copper being thus converted to the inorganic form and the content of solvent-soluble organic copper compound being reduced to a low value. The earlier experiments had shown that, in general, the weathering characteristics of such a duck, as measured by strength loss, fluidity increase, and loss in copper, are similar to those containing chromium, iron, and copper in inorganic form. In view of the hydrolytic process referred to above, this is not surprising. The increased retention of copper which the duck shows on weathering, with consequent maintenance of fungicidal properties together with the reduced actinic degradation imparted by the content of chromium oxide, renders this treatment valuable.

Copper 8-hydroxyquinolinolate ("copper-8") is known to be a potent fungicide, but, like copper naphthenate, is rapidly removed from cotton duck on weathering [3]. It was therefore of interest to examine the weathering characteristics of a mineral-dyed duck aftertreated with copper-8, applied in solubilized form [16] from solvent and also from a water dispersion of the compound. A similar investigation has been carried out with the copper salt of dehydroabietyl amine ("Rosin Amine D"), soluble form, elsewhere suggested as a textile fungicide [14].

The data are given in Table IV. It may be seen that the breaking strength losses of the two latter compounds were approximately the same as or somewhat less than that of the mineral-dyed control, which in turn showed a lower strength loss than the untreated control (see Table II). The copper naphthenate-treated samples showed breaking strength losses between those of the untreated control (Table II) and the copper-treated mineral-dyed fabric, but closer to the latter.

All of the treatments showed enhanced retention of copper, as compared with the almost total loss of metal which occurs with these compounds alone. The highest concentration of copper in the form of naphthenate and all of the copper-8 and copper-Rosin Amine D compound concentrations investigated imparted excellent resistance to soil-burial. The extent of actinic breakdown as judged by the increases in fluidity was markedly less with the copper-8 and Rosin Amine D compounds than with the untreated control ($\Delta F = 14.2$ rhes), but the fluidity increase values did not reach the strikingly low values (5–6) shown by some of the inorganic chromium-copper treatments described above.

The data obtained in this series suggest that copper-8 and copper-Rosin Amine D compound behave very similarly to copper naphthenate when applied in aftertreatments of mineral-dyed duck. In view of the more desirable characteristics of these compounds compared with copper naphthenate—*i.e.*, lower weight add-on and freedom from odor—their use in this way would seem to have considerable merit.

TABLE V. PROTECTIVE EFFECTS OF CHROMIC OXIDE AFTERTREATED WITH COPPER-8

Treatment Cr_2O_3	Treatment Cu as Cu-8	Method of application of Cu-8	Breaking strength loss on weathering (%)	ΔF on weathering (rhes)	Loss of copper (%)
1.75	—	—	23	10.9	—
1.08	—	—	25	9.8	—
	0.10	Solubilized, from solvent	25	7.0	82
	0.04	Solubilized, from solvent	28	8.7	87
	0.34	2-bath	27	11.8	92
1.41	0.09	Solubilized, from solvent	15	6.3	57
1.36	0.05	Solubilized, from solvent	15	7.7	45
0.91	0.10	Solubilized, from solvent	16	7.0	54
0.92	0.05	Solubilized, from solvent	18	6.6	58
1.42	0.31	2-bath	15	6.5	82
0.98	0.30	2-bath	15	6.6	85
Untreated control			39	14.0	—

(*c*) *Unbleached duck containing chromic oxide, copper-8, and mixtures of these.*—In view of the fact that the presence of iron in mineral-dyed duck does not seem to be a vital factor in the retention of copper, it was of interest to investigate the weathering characteristics of a duck containing chromic oxide aftertreated with an organic copper compound. A series of treatments with copper-8 in various amounts was therefore carried out on unbleached duck containing two levels (1.0% and 1.5%) of chromic oxide. The copper-8 was applied in two ways—*viz.*, solubilized from solvent solution, and by a two-bath method by successive impregnation with 8-hydroxyquinoline and copper sulfate. Samples containing similar amounts of copper-8, but no chromic oxide, were also prepared, together with the necessary controls containing chromic oxide only and untreated. The data are given in Table V.

It may be noted that the breaking strength losses on weathering are very similar for the samples carrying the single treatments with chromic oxide and with copper-8, it therefore being apparent that the copper-8 exerts a marked protective effect. In general, the breaking strength losses and fluidity increases for the untreated control and for the samples treated with chromic oxide alone were somewhat less than those for similar samples exposed during the previous summer (1952). The weather records for the two periods of exposure (see Table I) are very similar, with the exception that the rainfall during 1953 was somewhat less than during 1952. In this connection it is worth noting that, while the contribution of alternate wetting and drying to breaking strength losses of cotton fabrics, occurring during weathering, has not yet been quantitatively investigated, the work of Bone and coworkers [5] suggests that this effect may lead to appreciable strength losses.

The losses of copper from the samples containing copper-8 alone were large, this being in line with previous observations.

The samples which had the mixed treatments showed still lower strength losses and fluidity increases, the latter being similar to those shown by the mixed inorganic chromium-copper treatments (Table II). The losses of copper decreased sharply in the four samples containing chromic oxide and solubilized copper-8; with the two samples containing chromic oxide and copper-8 applied by the two-bath method, the losses of copper were the same as with the samples containing copper-8 alone, and no explanation of this can be offered.

The data for this series indicate that unbleached duck containing chromic oxide is capable of retaining copper from copper-8 to a greater extent than duck treated with copper-8 alone, and that the mixed treatment also affords enhanced protection against actinic breakdown of the cotton. In general, these effects are similar to those obtained with mixtures of chromic oxide and copper carbonate, but the latter treatments appear to show smaller losses of copper.

2. *Experiments with Lightweight Cellulosic Fabrics*

The rate at which cotton fabrics undergo loss in strength due to actinic breakdown in weathering increases as the thickness of the fabric decreases, owing to the fact that a greater proportion of the fibers receive direct exposure. In view of the protection

TABLE VI. EFFECT OF WEATHERING ON LIGHTWEIGHT FABRICS

Fabric	Treatment	2 Weeks Breaking strength loss (%)	*F*	4 Weeks Breaking strength loss (%)	*F*	6 Weeks Breaking strength loss (%)	*F*	8 Weeks Breaking strength loss (%)	*F*	Loss of copper (%)
Nainsook	none	7	6.6	18	9.7	23	12.6	26	15.7	—
	0.1% CuO + 0.1% Cr_2O_3	0	6.5	10	10.0	15	11.4	18	14.2	84
	0.5% CuO + 1.0% Cr_2O_3	0	4.7	9	6.4	14	10.8	16	12.6	79
Saponified acetate	none	37	2.2	52	3.7	64	4.7	71	5.8	—
	0.1% CuO + 0.1% Cr_2O_3	21	1.8	39	3.6	51	4.0	61	4.9	76
	0.5% CuO + 1.0% Cr_2O_3	21	1.2	37	1.7	48	2.7	51	3.1	78

NOTE: Cuprammonium fluidities were carried out on 0.5% dispersions in the case of the nainsook, and 2.0% dispersions with the saponified acetate.

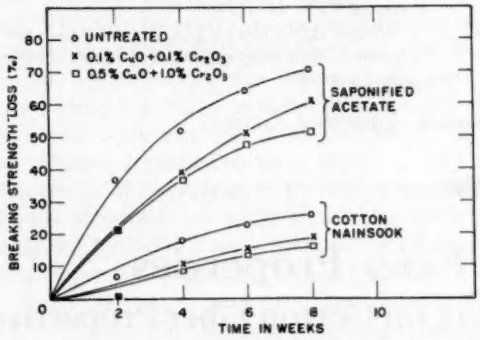

FIG. 2. *Effect of weathering on the breaking strength of lightweight cellulosic fabrics*

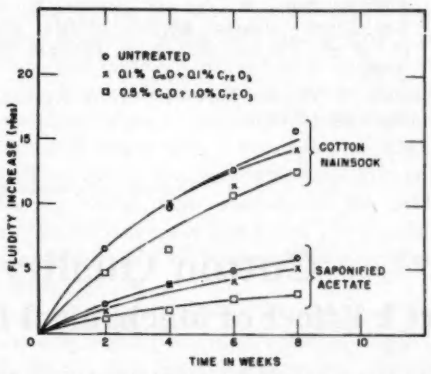

FIG. 3. *Effect of weathering on the cuprammonium fluidity of lightweight cellulosic fabrics.*

imparted to cotton duck by the chromium-copper treatments described above, it was of interest to determine whether this protective effect is also present with lightweight fabrics, which, in addition to a normally greater rate of actinic deterioration, also permit any treatments applied to them to be much more accessible to the effects of weathering.

The effect of a limited number of such treatments has been determined on a lightweight cotton nainsook and on a lightweight high-tenacity saponified acetate rayon fabric, two levels of treatment being used. The data given in Table VI and in Figures 2 and 3 show that over an exposure period of 8 weeks the protection afforded by the treatments, while marked, was considerably less than that obtained with the unbleached duck. Thus, for the saponified acetate at the higher level of treatment (0.5% CuO + 1.0% Cr_2O_3) the breaking strength loss was decreased by approximately 28% and in the nainsook by approximately 40%, compared with the untreated fabrics. The loss of copper was high, being approximately 80% for both fabrics, as compared with a value of 31% for unbleached duck which had been exposed, under similar conditions, for twice as long.

It is probable that, in the case of lightweight fabrics, the much greater accessibility of the treatments to leaching, as well as to mechanical removal in weathering, would make it necessary to apply a substantially higher level of treatment in order to maintain its protective action. However, in view of the above data, together with the lower degree of protection and the increased loss of copper shown by bleached duck as compared with unbleached duck, it is also believed that the better performance of the treatment in the latter case may be due to the capacity of the noncellulosic constituents of the unbleached duck to render the treatment less prone to removal by weathering. The possibility of this effect is being investigated further.

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Cotton Quality and Fiber Properties

Part I: Effect of Mechanical Blending on Cotton Fiber Properties*

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Abstract

A serious problem in single-fiber testing is the preparation of a homogeneous sample from which fibers may be selected in a random manner. Mechanical blenders, of the type developed for cotton by the U. S. Department of Agriculture, greatly improve the homogeneity of a bulk fiber sample. In the present work tests were made to show what changes in single-fiber properties result from the mechanical action of such a blender.

Relatively small changes in mechanical behavior of the cotton fibers were observed as a result of blending. With the conventional three passes through the blender a small decrease in breaking load (less than 10%) was found, with corresponding changes in breaking stress and energy to break. A reduction of fiber crimp with a slight increase in fiber length by the fiber array method was also noted.

Introduction

It has long been recognized that great differences exist between the properties of individual cotton fibers. Even fibers on the same seed differ from each other, and much larger differences exist between fibers from different bolls from various parts of the same plant. It is also known that cotton fibers which are associated in a single lock tend to remain associated in the same tufts through ginning, opening, picking, and even carding. The only way to obtain a representative sample for tests of fiber properties is to blend the fibers in the bulk sample

* A report of work done under contract with the U. S. Dept. of Agriculture and authorized by the Research and Marketing Act. The contract is being supervised by the Southern Regional Research Laboratory, Southern Utilization Research Branch, Agricultural Research Service.

so thoroughly that the fibers in these tufts are dispersed. Such blending is especially necessary if specimens for single-fiber tests are to be taken.

Various methods of blending have been described to overcome this problem [1]. For example, many laboratories have blended samples by hand. This method involves taking a fairly large number of pinches from the bulk sample, drafting each pinch into a long uniform strand, and forming a composite sliver which has fibers from each pinch at any cross section of its length. The procedure is tedious and time consuming, and does not necessarily result in a thorough blending of the fibers.

A number of mechanical blending machines have been described to aid in the blending operation [4, 5, 7, 9]. Of the several types, probably the most common is one in which the fibers are distributed on the surface of a drum covered with card or stripper clothing. One of the most recent and convenient of these machines is the mechanical cotton fiber blender developed by technologists of the U. S. Department of Agriculture [4]. The purpose of the present study was to evaluate the possibilities of using this blender for the preparation of cotton fiber samples prior to single-fiber testing.*

Three tests were performed to compare fibers obtained from the blender with those randomly selected from an unblended bulk fiber sample. The first of these (Test *1*) involved a study of the fiber length distribution after successive passes through the blender. The second (Test *2*) was concerned with the measurement of changes in the mechanical properties of fibers as a result of blending. Finally a confirmatory test (Test *3*) was performed with a second fiber type which was subjected to as many as ten passes through the blender in order to establish clearly any property changes which might take place.

Procedures

Blending

Two blenders were used in this study. Both followed the design described by Gaus and Larrison [4] of the Research and Testing Division, Cotton Branch, P.M.A., U.S.D.A. Their machine feeds a sample of cotton onto the surface of a wire-clothed cylinder to produce a bat in which the fibers are distributed at random in relatively thin layers. The procedure followed with the blender was essentially that recommended by the designers.

Tests for Fiber Length

Fiber length arrays for the various samples tested were made by the Fiber Laboratory of the Research and Testing Division, Cotton Branch, P.M.A., U.S. D.A. The methods employed were essentially those described in the A.S.T.M. Standards [2].

Fiber Selection

Fibers used for the determination of single-fiber mechanical properties were carefully pulled out from different positions of the bulk sample with a pair of tweezers and laid on a velvet board for later mounting. In some instances the fiber was classified at this point with respect to length by measurement of its stretched length with a steel rule. If it was also desired to classify the fiber with respect to cell-wall thickness, it was then examined in the field of a polarizing microscope with crossed Nicol prisms and a quarter-wave red or blue plate to give elliptically polarized light.

Some fiber samples were also prepared for fiber selection by sorting them into common length groups with the aid of a Suter-Webb sorter. In this case the fibers were taken from several positions within the desired length group in the fiber array; for it was found that, even after sorting, fibers tended to remain in the same family groups.

Single-Fiber Mechanical Properties

Fibers selected for test were mounted with Duco cement between two small brass tabs with approximately $\frac{1}{2}$ in. of fiber length between tabs. The tabs were about $\frac{1}{4}$ in. $\times$ $\frac{1}{4}$ in. and 0.005 in. thick. They could be cut to a known weight and reclaimed after a test merely by washing the cement off with acetone. They were used to apply tension to the fiber when separate vibroscope measurements were made as well as to hold the fiber for easy handling. Cellulose acetate tabs 0.015 in. thick were also used. These had the advantage of permitting microscopic examination of the fiber mount in the cement before or after testing, but they could not be used more than once. During the mounting the tabs were held with clips on a special mounting board which accommodates approximately 20 fibers.

* Blenders of this type may be purchased from Thwing-Albert Instrument Co., Pulaski Ave. and Penn St., Philadelphia 44, Pa., and from Custom Scientific Instruments, Inc., P.O. Box 170, Arlington, N. J.

All fibers tested for mechanical behavior were also individually vibroscoped [3, 8] in order to measure their weight fineness and approximate cross-sectional area. In the vibroscope method a length of fiber under tension is subjected to a transverse audio-frequency vibration and the conditions of resonance are observed. From these the average cross-sectional area of the fiber and the weight per unit length may be calculated.

In Test *2* the fibers, having been mounted between tabs, were individually tested in a vibroscope employing the variable frequency method and then put on a circular jig, which has been described by Evans and Montgomery [3]. The jig full of 50 or so fibers was then inserted into the Instron machine for measurement of the force-extension properties of the fibers (see Figure 1). For Test *3* the vibroscope arrangement was adapted to the Instron tester in such a way that the vibroscope test was performed simultaneously with the tensile test (see Figures 2 and 3). In this case, the method differed from that of Test *2* in that the frequency was kept constant and the tension and length at which resonance occurred were indicated by a pip on the force-extension record (see Figure 4).

All tests for mechanical properties were performed on the Instron tensile tester [6]. The conditions employed in these tests are summarized in Table I. A typical cotton fiber force-extension recording, such as that obtained from Test *3*, is shown in Figure 4. From this record and from the vibroscope cross-sectional area the following parameters were evaluated: breaking load, breaking elongation, Hookean

TABLE I. SUMMARY OF TEST CONDITIONS FOR DETERMINATION OF MECHANICAL PROPERTIES *

Test *2*	
Specimen length	$\frac{5}{8}$ in.
Vibroscope tension	100 mg.
Crimp test	
Crosshead speed	0.10 in./min.
Rate of elongation	16%/min.
Chart speed	50 in./min.
Load sensitivity	2.0 g. full scale
Break test	
Crosshead speed	0.12 in./min.
Rate of elongation	20%/min.
Chart speed	20 in./min.
Load sensitivity	10.0 g. full scale
Test *3*	
Specimen length	$\frac{1}{4}$ in.
Vibroscope tension	variable
Vibroscope frequency	3900 cycles/sec.
Crimp and break test	
Crosshead speed	0.05 in./min.
Rate of elongation	10%/min.
Chart speed	10 in./min.
Load sensitivity	2, 10, 20 g. full scale, changed during the test

* All tests were performed at 65% R.H., 70°F.

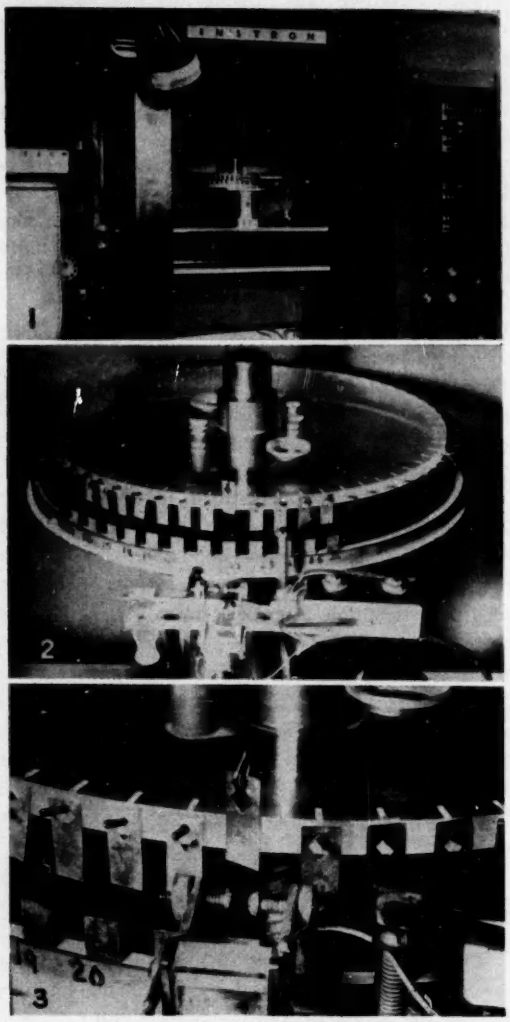

FIG. 1. *Instron tensile tester fitted with jig for single-fiber testing.*

FIG. 2. *Fiber jig with vibroscope attachment opened up to permit hooking of upper tab to load cell.*

FIG. 3. *Close-up of vibroscope attachment showing electrodes in place to excite fiber vibration during tensile test.*

slope, crimp energy, energy to break, elastic modulus, and breaking stress [3].

In Test *2* each fiber was first stretched to approximately 0.4 g. tension in a crimp test, then relaxed and allowed to rest for 24 hrs. before being extended to break in the tensile tester. In Test *3* the crimp test was performed at the same time as the tensile test, the load ranges being changed during the extension to break. The amount of energy required to extend the fiber to various points along the force-extension curves was determined by a mechanical integrator of the ball and disc type and registered automatically on the chart containing the force-extension record.

Data from the vibroscope and Instron charts were tabulated on special data sheets laid out to facilitate punching on an IBM punched card. All further calculations were performed on the cards using conventional IBM accounting equipment. Statistical summaries of the data were tabulated in a manner to facilitate analysis of variance of the various properties and factors being studied [10].

Test Pattern and Results

Test 1. *Effects of Blending on Fiber Lengths*

Two cottons were employed in studying the effect of mechanical blending on fiber length: an Amsak sample with a staple length of approximately $1\frac{3}{8}$ in. and an Empire cotton with the staple length of approximately $1\frac{3}{16}$ in. Five strips of sliver for each cotton were laid out parallel to make a large tow. This tow was then divided into four sections, each section weighing approximately 5 g. One section from each cotton was set aside as a control. Of the remaining three, one was blended with three passes through the blender at a normal setting of $\frac{1}{8}$ in. space between feed plate and blending cylinder; one was blended with six passes at the same setting; and one was blended with six passes at a close setting of $\frac{1}{16}$ in. Length arrays were obtained on all four samples for both cottons. Results are summarized in Table II.

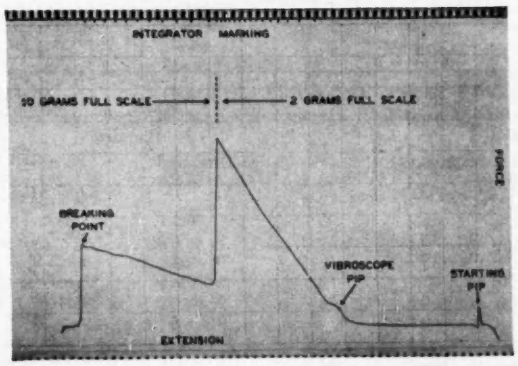

FIG. 4. *Force-extension record for a single cotton fiber showing vibroscope pip and integrator record.*

Test 2. Effects of Sorting and Blending on Mechanical Properties

The effects of sorting with a Suter-Webb sorter and blending with the mechanical blender on the mechanical properties of single fibers were determined on an Empire cotton. The test was conducted by two operators who selected and tested fibers in parallel. The statistical pattern used in this study is indicated in Table III.

In this test each operator selected fibers from four sources: (*1*) a bulk sample of unblended and unsorted cotton, (*2*) a sorted length array prepared from unblended cotton, (*3*) a bulk sample of blended cotton, and (*4*) a sorted length array prepared from blended cotton. The blending in this test consisted of three passes through the mechanical blender at the normal setting. The sorting was carried out in the manner usually employed to prepare a length array. Each operator after selecting fibers from one of these sources classified it with respect to length. If the fiber belonged to either the upper quartile length group ($1\frac{3}{16}$ in.) or the mean length group ($1\frac{5}{16}$ in.), the fiber was then examined in the polarizing microscope in order to classify it as being mature or immature. All fibers examined were classified. The method of classification was essentially that described in the A.S.T.M. Standards [2]. Each operator kept a record of the number of fibers examined in order to compare similarity of classification between the two operators.

The fibers were then mounted, vibroscoped, and tested for crimp and tensile properties. Due to limitations of time and space, tests were performed in three days to make up the total number of fibers indicated in the statistical pattern. The two operators scheduled their work to perform the mounting, vibroscoping, and tensile testing operations on the same days. Three fibers from each combination in the statistical pattern (Table III) were tested daily by each operator.

The results were subjected to factorial analysis for each fiber property in order to determine the effects of blending, sorting, maturity, length, and

operator techniques. Effects found to be significant at the 5% level or less are shown in Table IV. Mean values of fiber properties for the main fiber groups may be found in Table V.

In the maturity classification, Operator 1 tended to put borderline fibers in the immature class with the result that the average cross-sectional area found for his immature group was higher than that of Operator 2. Operator 2, on the other hand, put the borderline fibers into the mature class. Since the maturity of the original sample was the same for both operators and equal numbers of fibers were to be tested, Operator 2 had to examine more fibers to find the requisite number of immature ones. The differences between operators, therefore, tended to be due to sample maturity with the result that rather strong operator-by-maturity interactions were found in the factorial analysis. The effect which this selection had on fiber properties is shown in Table VI.

Test 3. Effect of Successive Passes Through the Blender

In this test all functions of fiber selection, mounting, and tensile testing were performed by the same operator. A sample of Acala 4–42 cotton was divided into three parts. One part was set aside as a control; one part was passed through the blender three times; the third part was passed through the

TABLE II. CHANGES IN FIBER LENGTH WITH BLENDING*

	Weight % of all fibers					
	Empire Cotton			Amsak Cotton		
Length group ($\frac{1}{16}$-in. increments)	0 Passes	6 Passes, normal setting†	6 Passes, close setting‡	0 Passes	6 Passes, normal setting†	6 Passes, close setting‡
29	—	—	—	1.20	1.58	2.15
27	—	—	—	7.53	6.78	8.15
25	—	—	—	13.59	13.42	15.81
23	0.36	1.92	1.02	14.65	15.71	15.36
21	5.31	5.80	6.23	15.59	16.02	13.93
19	14.24	14.98	18.42	10.74	10.70	12.18
17	28.62	26.12	23.26	8.82	8.28	6.94
15	15.49	14.58	16.86	6.46	6.12	5.82
13	10.62	11.10	10.28	5.52	5.63	5.02
11	7.68	7.53	6.58	3.43	4.09	4.03
9	5.94	6.38	5.87	4.32	3.57	3.18
7	4.73	5.13	5.16	2.76	3.87	2.64
5	3.84	3.57	4.09	2.63	1.94	2.87
3	2.32	1.87	1.65	1.74	1.45	1.43
Upper quartile length	1.10	1.12	1.13	1.46	1.48	1.51
Mean length	0.90	0.91	0.92	1.16	1.18	1.21
Coeff. of variation (%)	31	32	31	34	33	32

* Results of U.S.D.A. Cotton Fiber and Spinning Laboratory Tests Nos. W-448 and W-452.
† A space of $\frac{1}{8}$ in. between feed roll and cylinder wire.
‡ A space of $\frac{1}{16}$ in. between feed roll and cylinder wire.

TABLE III. STATISTICAL PATTERN FOLLOWED IN TEST 2*

	Unblended				Blended			
	Unsorted		Sorted		Unsorted		Sorted	
Operator:	O_1	O_2	O_1	O_2	O_1	O_2	O_1	O_2
Upper quartile length fibers								
Mature	9†	9	9	9	9	9	9	9
Immature	9	9	9	9	9	9	9	9
Mean length fibers								
Mature	9	9	9	9	9	9	9	9
Immature	9	9	9	9	9	9	9	9

* Empire cotton fibers, upper quartile length $1\frac{3}{16}$ in., mean length $\frac{13}{16}$ in.
† Each "9" represents nine single-fiber replicates. Each main effect is thus established by tests on 144 fibers in each group and first-order interactions are established by tests on 72 fibers in each group.

blender ten times. In all cases the blender setting was normal.

Fibers were selected at random from each of the three groups, the only requirement being that they exceed approximately $\frac{3}{4}$ in. in length. Tests were carried out on four days, sixteen fibers from each of the three groups being tested on each day.

The results were subjected to a factorial analysis on each fiber property. The mean values of fiber properties and coefficients of variation after 0, 3, and 10 passes are shown in Table VII.

Discussion

It can be seen from the results of Test *1* that no appreciable changes in length or length distribution occur as a result of blending up to six passes at the normal setting of the blender. When the setting is reduced to $\frac{1}{16}$ in., six passes result in a small increase in length of the longer fibers in the sample. The effect of this increase is to raise the upper quartile and mean length 0.01–0.03 in. No evidence of fiber breakage as a result of blending action was obtained in this test.

It is doubtful if the small changes in length caused by the action of the blender can be due to an actual stretching of the fibers. The increases in length are more likely due to changes in the crimp of the fiber. Such crimp is known to be pulled out by relatively low tensions and, although the effects of blending on crimp energy in Tests *2* and *3* were not statistically significant, in both tests the crimp energy was reduced as a result of blending action. Possibly one of the reasons for the small effects in fiber crimp is that if the fiber is released after stretching, at least

TABLE IV. SUMMARY OF FACTORIAL ANALYSIS OF TEST *2* *

	Significance levels									
	Factor					Interaction †				
Fiber properties	Maturity	Blending	Operator	Sorting	Length	M×O	M×L	B×S	S×L	L×O
Area of cross section	0.1%	—	1 %	2%	—	0.1%	—	4%	4%	3%
Breaking load	0.1	—	0.1	1	—	2	—	—	—	—
Breaking elongation	4	4.5%	—	—	—	—	—	—	—	—
Hookean slope	0.1	—	0.1	—	—	0.1	3%	—	—	—
Crimp energy	0.1	—	—	1	—	0.1	—	—	—	1
Energy to break	0.1	4	—	—	—	—	—	—	—	5
Elastic modulus	0.1	—	1	—	4%	—	—	—	—	—
Breaking stress	5	5	—	1	—	—	—	—	—	—

* Effects found to be significant at the 5% level or better.
† The M×B, B×L, B×O, S×O interactions showed no significant differences at the 5% level.
A dash (—) indicates no significant difference at the 5% level.

TABLE V. MEAN VALUES OF FIBER PROPERTIES FOR MAIN FIBER GROUPS IN TEST *2* *

	Property and units							
	Area of cross section ($cm.^2$)	Breaking load (g.)	Breaking elongation (%)	Hookean slope (g./1%)	Crimp energy (g. cm./cm.)	Energy to break (g. cm./cm.)	Elastic modulus ($g./cm.^2/100\%$)	Breaking stress ($g./cm.^2$)
Mature	1.551×10^{-6}	3.66	5.31	0.788	1.91×10^{-3}	114×10^{-3}	51.4×10^{6}	2.53×10^{8}
Immature	0.921	1.94	6.08	0.366	0.87	69	41.1	2.33
Unblended	1.241	2.93	6.07	0.572	1.42	100	45.3	2.54
Blended	1.230	2.66	5.32	0.582	1.36	83	47.2	2.32
Unsorted	1.277	2.66	5.42	0.581	1.58	85	44.7	2.23
Sorted	1.194	2.93	5.96	0.572	1.20	99	47.8	2.63
Mean length	1.256	2.71	5.79	0.548	1.47	93	43.8	2.33
U.H.M. length	1.216	2.89	5.59	0.606	1.31	91	48.8	2.53
Operator 1	1.301	3.05	5.83	0.634	1.21	101	49.0	2.55
Operator 2	1.171	2.56	5.55	0.520	1.57	83	43.6	1.97

* 144 fibers in each group.

part of the crimp returns in time. A more effective test of the effect of blending on crimp might be to measure crimp energy as a function of time after blending.

In this connection it is of interest to note that sorting has a very pronounced effect on the crimp energy of the fibers. This was clearly shown in Test *2* in which sorting produced a main effect significant at the 1% level, despite the fact that the coefficient of variation of crimp energy is as great as 60%. Sorting caused a reduction of 30% of the energy necessary to uncrimp the fibers.

In both Tests *2* and *3* blending resulted in small reductions in breaking load, breaking elongation, breaking stress, and energy to break. Since all four of these parameters are interrelated it is probable that the real effect was merely a reduction in the breaking load of the fiber. Such a change would produce a shortening of the stress-strain curve and, thus, affect the other properties in the same way. The slope of the curve and the elastic modulus were not changed as would have been the case if a mechanical "conditioning" had taken place. The effect of blending on breaking load of the single fibers is, therefore, probably due to local weakening of the fibers. It has been shown that there are many points of weakness along the length of cotton fibers [11], and it seems quite possible that in the blending action some of these places are damaged in some way or other.

It might be expected that homogenizing the bulk sample by blending ten times, as in Test *3*, would cause a change in the dispersion of the property values obtained. Such a change would occur, however, only if the fibers tested for zero passes were not representative of the unblended sample. Actually, in this test pains were taken to make the fiber samples truly representative so that differences in means would reflect the action of the blender on the fibers. The similarity of the coefficients of variation for 0, 3, and 10 passes, shown in Table VII, indicate that differences between the means are probably not caused by differences in representation obtained in the three cases.

TABLE VI. EFFECT OF OPERATOR SELECTIONS ON FIBER PROPERTIES IN TEST *2*

A. Maturity selections

	Mature	Immature
Operator 1	256 (59%)	179
Operator 2	267 (68%)	124

B. Mean values of fiber properties for mature and immature fiber groups by operators (each operator mean is for 72 fibers)

	Operator 1	Operator 2
Area of cross section ($\times 10^{-6}$ cm.^{2})		
Mature	1.552	1.549
Immature	1.050	0.792
Breaking load (g.)		
Mature	3.85	3.47
Immature	2.24	1.63
Breaking elongation (%)		
Mature	5.64	4.98
Immature	6.02	6.13
Hookean slope (g./1%)		
Mature	0.826	0.750
Immature	0.442	0.290
Crimp energy (g. cm./cm. $\times 10^{-3}$)		
Mature	1.51	2.30
Immature	0.92	0.83
Energy to break (g. cm./cm. $\times 10^{-3}$)		
Mature	247	209
Immature	156	120
Elastic modulus ($\times 10^6$ g./cm.^{2}/%)		
Mature	0.541	0.488
Immature	0.440	0.383
Breaking stress ($\times 10^8$ g./cm.^{2})		
Mature	2.70	2.36
Immature	2.41	2.25

TABLE VII. EFFECT OF SUCCESSIVE PASSES THROUGH THE BLENDER ON FIBER PROPERTIES IN TEST *3* *

Property and units	No. of passes 0	3	10	Statistical significance level of "passes" in factorial analysis
Area of cross section ($\times 10^{-6}$ cm.^{2})	1.369 (24)	1.368 (27)	1.314 (22)	10%
Breaking load (g.)	5.74 (48)	5.50 (48)	4.70 (48)	5%
Breaking elongation (%)	8.93 (38)	9.74 (40)	8.44 (38)	10%
Hookean slope (g./1%)	0.569 (44)	0.530 (49)	0.509 (47)	10%
Crimp energy (g. cm./cm. $\times 10^{-3}$)	0.95 (74)	0.85 (55)	0.39 (56)	10%
Energy to break (g. cm./cm. $\times 10^{-3}$)	121 (55)	124 (56)	100 (59)	10%
Elastic modulus ($\times 10^6$ g./cm.^{2}/%)	0.407 (37)	0.385 (43)	0.384 (41)	10%
Breaking stress ($\times 10^8$ g./cm.^{2})	4.16 (42)	4.01 (39)	3.57 (42)	10%

* Mean value and coefficients of variation (in parenthesis) of fiber properties (64 fibers in each mean).

The effect of sorting and the interaction of blending by sorting on the area of fiber cross section in Test *2* probably arise from the fact that the areas were determined by the vibroscope method using a constant tension of 100 mg. This tension was probably not enough to remove all of the crimp from the fiber. Pretreatment which caused a reduction in the energy to uncrimp the fibers thus also caused an apparent decrease in the weight of fiber for a given length between tabs. The fibers from the sorted and blended group, therefore, had the lowest area.

The sorting operation in Test *2* also produced a 15% increase in fiber breaking load and breaking stress. This increase is probably due to a mechanical "conditioning" effect induced by the stretching of the fibers in the sorting procedure—the same stretching which caused the lowering of the fiber crimp already noted. It should be pointed out that there is considerable latitude in the extent of fiber manipulation required to prepare a good sort. It seems altogether possible that some operators might be able to make a fiber sort without producing the changes in fiber properties herein noted.

Conclusions

The results outlined above show that the changes produced on cotton fibers by the mechanical blender in homogenizing the fiber sample are not large. Most serious is the reduction in single-fiber breaking load which is somewhat less than 10% with three passes through the blender. This observation emphasizes the need for limiting the physical handling of the cotton as much as possible prior to single-fiber testing.

It has also been demonstrated that the sorting of cotton fibers wih the aid of a Suter-Webb sorter may produce a considerable decrease in fiber crimp and increases in breaking load and breaking stress of the fibers. A separate investigation must be made to show whether or not these changes in fiber properties can be avoided by proper fiber manipulation.

Acknowledgments

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The Effect of Time and Temperature of Presoaking and the Temperature of Acetylation on the Rate and Degree of Acetylation of Cotton Fibers

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Introduction

In recent years considerable attention has been focused on the use of partially acetylated cotton as a textile fiber. The chemical modification of cotton by partial acetylation imparts many new and valuable properties to the cotton fiber while its physical appearance and general textile qualities remain virtually unchanged. The new characteristics of the chemically modified cotton fibers include resistance to mildew and microbiological rotting; resistance to the effects of high temperature and continued heat; low moisture regain and high electrical resistance, as compared with untreated cotton; and resistance to coloring with many direct dyes [2].

Extensive investigation has been carried out on partially acetylated cotton in order to determine more about the new properties imparted to the cotton fiber. The Department of Agriculture, through its Southern Regional Research Laboratory, New Orleans, La., conducted extensive research in the production and uses of acetylated yarn and fabrics.

It was the purpose of this study to determine (*1*) the effect of the time and temperature of presoaking on the rate and degree of acetylation of different varieties of cotton fibers with the time and temperature of the acetylation held constant and (*2*) to study the effect of the acetylation temperature on the degree of acetylation under constant conditions of presoaking.

Acetylated cotton, on a commercial scale, must necessarily be produced by a continuous process carried out within the shortest possible time with the least amount of damage to the fibers. Heuser [7] showed that the amount of degradation of cellulose depends upon the time and temperature of acetylation, independently of the acetyl values reached. Therefore, it is of prime importance to determine some method by which the time and temperature of acetylation could be reduced and the desired acetyl values obtained. To that end various conditions of time and temperature of presoaking and temperatures of acetylation were studied, the acetyl content was determined, and the results were analyzed.

Theoretical Considerations

The acetylation of cotton fibers with glacial acetic acid alone occurs very slowly, even under the effects of high temperatures. Malm and Clark [9] boiled surgical cotton in glacial acetic acid, and at the end of 96 hrs. only 6.2% acetyl content was reached. Even after 500 hrs. only 6.4% acetyl content was obtained, and considerable degradation of the fibers resulted. In sealed glass tubes at 140°–145°C, 7.5% acetyl content was obtained after 48 hrs. Again the long time and high temperature led to considerable degradation. The use of acetic anhydride in place of glacial acetic acid resulted in greatly increased acetyl content, 38.26% at 118°C, but again the cellulose was considerably degraded [4].

The acetylation reaction is greatly facilitated by the use of certain catalysts, such as sulfuric and perchloric acids, which are actually dehydrating agents although they do not seem to act as such when acetic anhydride is used for acetylation. The function of the catalyst is not clearly understood. One theory advanced in the case of sulfuric acid is that the acid reacts with the acetic anhydride to form acetylsulfuric acid, which functions as the acetylating agent and regenerates sulfuric acid to form a complete cycle. The chief function of the sulfuric acid seems to be as an aid in the swelling of the cellulose material [5].

In this study perchloric acid, which is the most powerful catalyst for the acetylation of cellulose [6],

* A condensation of Mr. Owens' thesis as partial fulfillment of the requirement for his degree of Master of Science in Textile Engineering.

was used. In acetic acid/acetic anhydride systems, strong acids such as perchloric acid exhibit "superacidity" which may be accounted for by postulating the existence of highly acidic ions, and in this respect perchloric acid is stronger than sulfuric acid [8].

The rate of acetylation is greatly influenced by the moisture content of the cellulosic material. The rate of reaction increases with increasing moisture content until the maximum is reached at about 25% to 30%. The increasing water content causes the capillaries of the fibers to enlarge, which favors the diffusion of the acetylating mixture into the inner parts of the fiber. When the moisture content reaches 25% to 30%, the fibers have reached saturation—*i.e.*, all capillaries are filled with water—so that further increase of water content has no effect upon the diffusion and, hence, upon the rate of reaction. Any compound which enlarges the lattice spacings and permits faster diffusion into the crystallite increases the reaction rate [12].

Presoaking with glacial acetic acid has the same general effect as presoaking in water. The use of glacial acetic acid is preferred in the partial acetylation of cotton as water must be completely removed prior to acetylation. Pretreatment with glacial acetic acid or water shortens the time necessary to reach a certain acetyl content, and thus the degradation of the cellulose is reduced and the molecular weights of the acetates are higher.

The acetylation of cellulose is a heterogeneous reaction due to both fiber and micellar structure. X-ray studies have shown that in the acetylation of cellulose the reagent penetrates the fiber, attacking first the surface of the micelle which is changed into the triacetate and then proceeds inwards, producing between the unreacted interior and the completely reacted surface a partially reacted area in which only one or two hydroxyl groups have been replaced [11]. In the crystalline structure where the cellulose chains are densely packed and regularly oriented, the reaction is slow. In the amorphous portion of the fiber, where access of the reagents is greater because of the expanded structure, the reaction is much faster. No definite border exists between these regions, but transitional regions exist in an intermediate degree [10]. Thus, the amorphous regions are accessible for chemical reactions as well as are the surfaces of the crystalline regions [13]. X-ray studies indicate the crystalline fraction of cotton to be 70% within small experimental error [3].

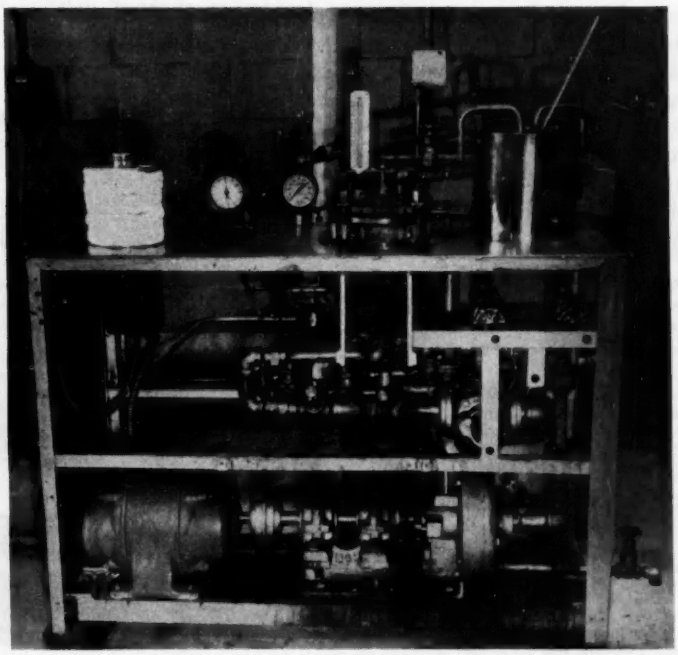

FIG. 1. *Front view of the acetylation machine.*

Experimental Procedure

Six different varieties of raw cotton were selected for this study. These cottons were chosen to represent a wide range of physical properties, such as maturity, fiber fineness, and tensile strength as illustrated in Table I.

In the first part of this study, the cottons were acetylated under uniform conditions of time and temperature—*i.e.*, 45 min. at 64°F—with the time and temperature of presoaking as variables. The times used were 10, 30, 60, 120, and 240 min., and the temperatures selected were 70°F, 100°F, 130°F, and 170°F.

In the second part of this study, the time and temperature of presoaking were held constant at the optimum conditions of presoaking as determined from part *I*. The acetylation temperatures were varied with the time of acetylation being held constant at 45 min. The temperatures used in the acetylation were 58°F, 64°F, 70°F, 76°F, and 82°F.

All acetylations and presoakings were carried out in a one-pound-package dyeing machine modified in such a manner that the above temperatures were easily obtainable and held constant (Figures 1 and 2). This modification consisted of adding cooling coils in series with the pipes carrying the liquid to the reaction chamber. Valves were placed in the pipe lines so that the cooling coils could be cut off from the main lines if desired. The cooling coils were placed in a large reservoir or tank in which ice and/or water could be placed. The machine was thoroughly rinsed out with used acetylation mixture prior to adding the conditioned cotton in order to be certain that the machine was free of water. The cotton to be acetylated was placed on a stainless steel spindle, and stainless steel screens were placed between each variety of cotton. Six 25-g. samples plus 90 g. of filler cotton or twelve 20-g. samples were placed in the machine at a time. The total weight of cotton used was kept constant at 240 g. Sixteen liters of glacial acetic acid were added after the cotton was placed in the machine. The valves were so adjusted that the cooling coils were filled with acid and could be used if so desired. The acid was adjusted to flow inside-out. The reacting chamber was steam jacketed, and after the machine was filled with acid, the steam (40 lbs. pressure) was turned on and the acid quickly brought up to the desired presoaking temperature. The thermometer on the acetylating chamber cover was used in determining the presoaking temperature. When the desired time of presoaking was reached, the presoaking acid was quickly cooled to 80°F through the use of the cooling coils. The cooling coils were packed with ice and water just prior to the end of the presoaking period. When the temperature of the presoaking solution reached 80°F, it was quickly drained from the machine into a five-gallon acid carboy and set aside to be used for the next acetylation mixture.

TABLE I. SUMMARY OF PHYSICAL AND CHEMICAL PROPERTIES OF THE ORIGINAL COTTON FIBERS

Cotton	Micronaire (mg./in.)	Pressley index	X-ray angle 40%*	Maturity NaOH method* (%)
Memphis	2.45	7.15	37.92	38
Empire Bale 92, Bale 249290	3.70	7.30	34.08	72
Bob Shaw	5.10	8.42	31.32	88†
Stoneville 2B	3.20	8.07	31.20	80
Acala 1517	4.00	8.93	29.76	86
Lockett 140	5.67	7.51	36.18	92

* These results were furnished by the Southern Regional Research Laboratory, New Orleans, La.

† Maturity was determined by the Arealometer.

Acetylation

Preparation of the Acetylation Mixture

The acetylation mixture was composed of three parts of glacial acid, one part of acetic anhydride,

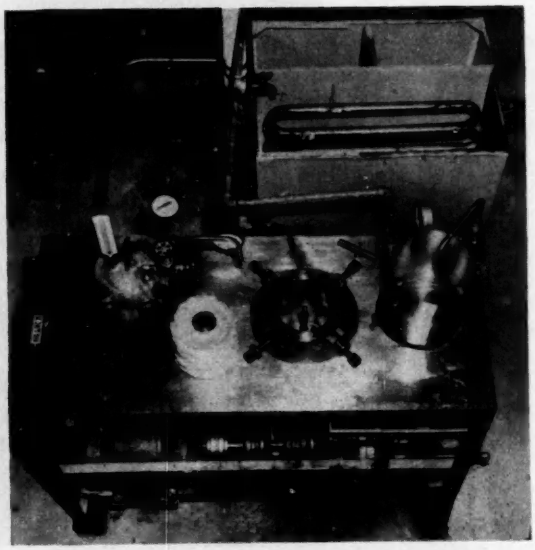

FIG. 2. *Top view of the acetylation machine.*

and 0.15% of perchloric acid, based on the total volume of acid and anhydride. The total volume of acetylation mixture used in the machine consisted of 12.6 l. of glacial acetic acid, 4.2 l. of acetic anhydride, and 25.5 cc. of perchloric acid. At least 12 hrs. prior to acetylation the acetic anhydride was added to 11.6 l. of acetic acid, and the mixture was allowed to stand in order that any water in the acid would be converted into acetic acid by reaction with the anhydride. The final acetylation mixture was made up just prior to the acetylation. The acid-anhydride solution was cooled to 50°F before the catalyst was added. The perchloric acid was mixed with the remaining liter of acetic acid and slowly added, with agitation, to the cooled acid-anhydride solution. There was an initial temperature rise of about 4°F–8°F when the perchloric acid was added, after which the mixture was again cooled to 50°F.

Acetylation

Upon completion of presoaking and after draining the machine of the acid the acetylating mixture was added to the machine through the reserve tank. The valve to the cooling coils was opened, and the acetylating solution was pumped through the coils. The valves to the cooling coils were manipulated in such a manner that the temperature was held constant during the acetylation. All acetylations were carried out for 45 min., at the end of which time the acetylation mixture was quickly drained and the cotton thoroughly washed. In part *I* of this study, the temperature of acetylation was held constant at 64°F, and in part *II* the temperature was varied in six-degree increments from 58°F to 82°F for the different acetylations.

Treatment After Acetylation

After the machine was drained, the samples were washed with cold water. The washing was continued for 30 min. after which the machine was drained. The machine was again filled with water, and 50 cc. of concentrated ammonium hydroxide was added and circulated through the cotton for about 10 min. or until tests with litmus paper indicated the wash water was basic. The machine was again drained and cold water added.

Testing After Acetylation

Physical Properties

Physical properties such as moisture content, fiber fineness, and fiber strength of the acetylated cottons were determined on the conditioned fibers by use of the Brabender moisture tester, the Sheffield Micronaire, and the Pressley fiber tester.

Analysis for Acetyl Content

Two to three grams of the conditioned samples of acetylated cotton were carefully handpicked from the original 20- or 25-g. samples and ground up in the Wiley Mill. They were then transferred into tared 250-ml. Erlenmeyer flasks. The flasks were again accurately weighed, and the exact weight of the samples was calculated. From the percent moisture previously determined, the dry weight of the samples was calculated. Fifty milliliters of 75% methyl alcohol were added to each sample and heated for 15–20 min. at 140°F. Fifty milliliters of approximately 0.5*N* sodium hydroxide solution were then added to each flask, and the flasks again heated to 140°F and allowed to stand 12 to 24 hrs. before titrating. Two blanks of unacetylated cotton were included with each set of samples and carried through the same procedure. Two to three drops of phenolphthalein were added to the flasks as an indicator, and the saponified samples were then titrated with approximately 0.5*N* hydrochloric acid until the pink color disappeared. If the pink color reappeared on standing, more acid was used until the solution was completely neutralized. The percentage of acetyl content was then calculated according to the following equation:

$$\% \text{ acetyl content} = \frac{(\text{cc. acid used by blank}) - (\text{cc. acid used by sample})}{\text{dry weight of the sample}} \times 4.302 \times N,$$

where 4.302 is the milliequivalent weight of the acetyl group times 100 and N is the normality of the hydrochloric acid.

Dye Test for Evenness of Acetylation

The uniformity of acetylation is determined qualitatively by a dyeing test. The dried samples (or portions thereof) were dyed with a solution containing 4% Chlorantine Fast Blue 3RRL, 4% Celleton Fast Yellow RRA, and 5% Triton X-100 calculated on the weight of the sample. From the results of this test the evenness of the acetylation could be readily observed.

Discussion of Results

In part *I* of this study, the effect of time and temperature of presoaking on the rate and degree of

acetylation was determined. The acetyl contents obtained at different times and temperatures are shown in Tables IV–VII and Figures 3 through 6.

A study of these data indicated that the temperature of the presoaking acid had a very marked effect on the degree of acetylation. It can be seen that as the temperature was increased, particularly at the shorter presoaking periods, the degree of acetylation rapidly increased. This may be illustrated in the case of Acala 1517 cotton, as shown in Table II and also shown in Figures 8 through 12, as well as in the case of the other more mature fibers.

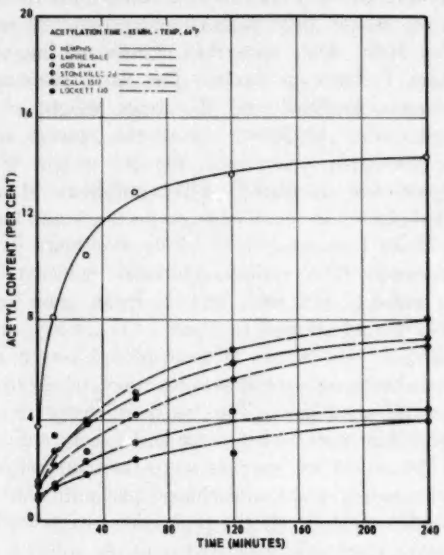

FIG. 3. *The change in acetyl content with presoaking time at 70°F.*

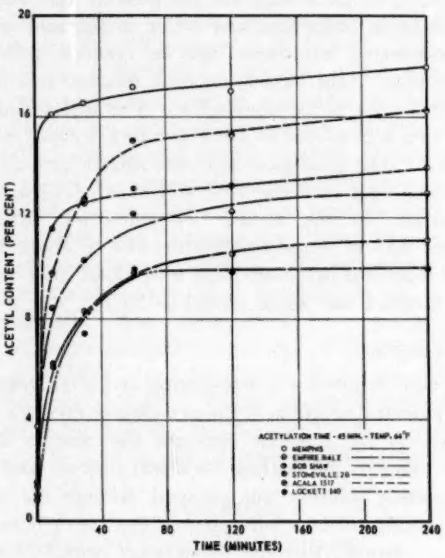

FIG. 5. *The change in acetyl content with presoaking time at 130°F.*

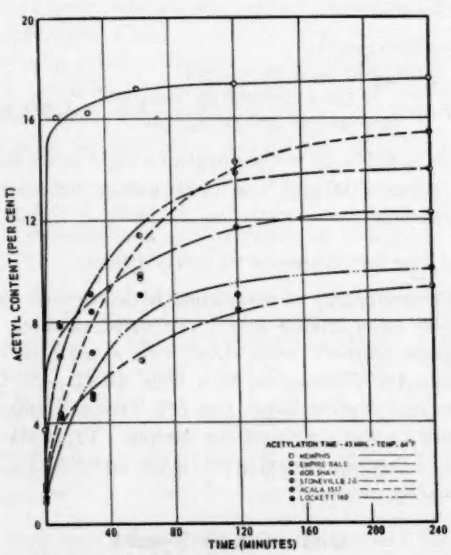

FIG. 4. *The change in acetyl content with presoaking time at 100°F.*

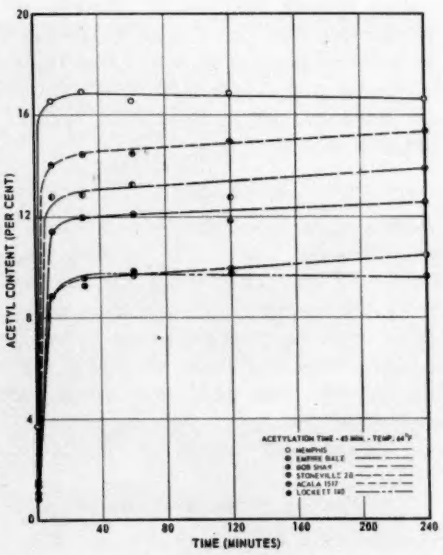

FIG. 6. *The change in acetyl content with presoaking time at 170°F.*

TABLE II. A COMPARISON OF THE ACETYL CONTENT OF ACALA 1517 COTTON AT VARIOUS TIMES AND TEMPERATURES OF PRESOAKING

Temperature (°F)	10 min. (% acetyl)	30 min. (% acetyl)	60 min. (% acetyl)
70	2.16	2.78	4.20
100	6.61	6.78	9.75
130	9.80	12.73	15.05
170	14.01	14.45	14.42

TABLE III. A COMPARISON OF THE ACETYL CONTENT OF VARIOUS COTTON FIBERS PRESOAKED AT 70°F FOR DIFFERENT TIMES

Cotton	240 min. (70°F)	18 hrs. (70°F)
Memphis	14.44	16.75
Empire Bale 92	7.27	10.75
Bob Shaw	4.42	8.27
Stoneville 2B	8.03	12.23
Acala 1517	6.93	10.97
Lockett 140	4.00	8.56

As the time of presoaking increased, the effect of the temperature decreased with the exception of the 70°F run. This is shown by the fact that at 100°F the acetyl content reached a maximum in about 120 min., at 130°F in about 60 min., and at 170°F in about 30 min. This was true for all the cottons with the exception of the immature Memphis cotton which reached its maximum acetyl content in 10 min. at the three higher temperatures. After the maximum was attained, there were only slight fluctuations in acetyl content with time of presoaking, which may be attributed to small variations in the cotton, experimental error, etc. The maximum degree of acetylation for each variety of fiber was approximately the same for all three of the higher temperatures. For example, the acetyl content of the immature Memphis cotton reaches its maximum acetylation in 10 min. and then only varies from a low of 16.07% acetyl at the 10-min., 170°F presoak to a high of 17.99% at the 240-min., 130°F presoak, a difference of less than 2%, while the most mature cotton, Lockett 140, reached its maximum at 60 min. and varied from a low of 9.04% acetyl content at the 60-min., 100°F presoak to a high of 10.06% acetyl content at the 240-min., 100°F presoak, a difference of 1%.

The maximum acetyl content was never established at 70°F within the time range studied as shown in Table III. The acetyl content was still increasing at the end of 240 min. for all the varieties of cotton and the degree of acetylation for the various times was considerably below that of the other temperatures. With the exception of the most immature fibers, Memphis and Empire Bale 92, the acetyl content at the end of 240 min. was only about half the maximum obtained. The same varieties of conditioned cotton were presoaked for 18 hrs. at 70°F by Blandin [1], and a comparison of his re-

TABLE IV. EFFECT OF TIME OF PRESOAKING AT 70°F ON THE DEGREE OF ACETYLATION *

Cotton	0 min.	10 min.	30 min.	60 min.	120 min.	240 min.
Memphis	3.72	8.06	10.50	13.05	13.74	14.44
Empire Bale 92	1.52	2.75	3.83	5.07	6.25	7.27
Bob Shaw	0.86	1.46	2.35	3.07	4.38	4.42
Stoneville 2B	1.37	3.36	3.97	4.87	6.80	8.03
Acala 1517	1.43	2.16	2.78	4.20	5.61	6.93
Lockett 140	1.02	1.33	1.84	2.48	2.68	4.00

* All acetylations in Tables IV–VII were carried out at 64°F for 45 min.

TABLE V. EFFECT OF TIME OF PRESOAKING AT 100°F ON THE DEGREE OF ACETYLATION

Cotton	0 min.	10 min.	30 min.	60 min.	120 min.	240 min.
Memphis	3.72	16.07	16.21	17.20	17.33	17.52
Empire Bale 92	1.52	7.87	9.10	9.86	11.77	12.27
Bob Shaw	0.86	4.38	4.92	6.44	8.45	9.34
Stoneville 2B	1.37	7.90	8.40	11.45	13.78	14.00
Acala 1517	1.43	6.61	6.78	9.75	14.30	15.40
Lockett 140	1.02	4.24	5.10	9.04	9.06	10.06

TABLE VI. EFFECT OF TIME OF PRESOAKING AT 130°F ON THE DEGREE OF ACETYLATION

Cotton	0 min.	10 min.	30 min.	60 min.	120 min.	240 min.
Memphis	3.72	16.11	16.53	17.17	17.00	17.99
Empire Bale 92	1.52	8.42	10.35	12.14	12.25	12.99
Bob Shaw	0.86	6.07	8.30	9.87	10.55	11.10
Stoneville 2B	1.37	11.58	12.59	13.18	13.28	14.00
Acala 1517	1.43	9.80	12.73	15.05	15.30	16.24
Lockett 140	1.02	6.20	7.41	9.91	9.82	9.96

TABLE VII. EFFECT OF TIME OF PRESOAKING AT 170°F ON THE DEGREE OF ACETYLATION

Cotton	0 min.	10 min.	30 min.	60 min.	120 min.	240 min.
Memphis	3.72	16.51	16.95	16.51	16.82	16.60
Empire Bale 92	1.52	11.41	11.95	12.08	11.82	12.53
Bob Shaw	0.86	8.89	9.52	9.62	9.95	10.45
Stoneville 2B	1.37	12.79	12.81	13.25	12.71	13.88
Acala 1517	1.43	14.01	14.45	14.42	14.96	15.36
Lockett 140	1.02	8.86	9.27	9.81	9.75	9.63

TABLE VIII. EFFECT OF TEMPERATURE OF ACETYLATION ON THE DEGREE OF ACETYLATION *

Cotton	58°F	64°F	70°F	76°F	82°F
Memphis	12.69	16.51	19.22	20.71	23.68
Empire Bale 92	9.12	11.41	13.51	17.10	20.36
Bob Shaw	7.48	8.89	10.68	15.30	19.28
Stoneville 2B	10.68	12.79	15.40	18.31	21.51
Acala 1517	10.76	14.01	16.77	20.03	23.12
Lockett 140	7.96	8.86	10.98	14.72	19.88

* Presoaked for 10 min. at 170°F and acetylated for 45 min.

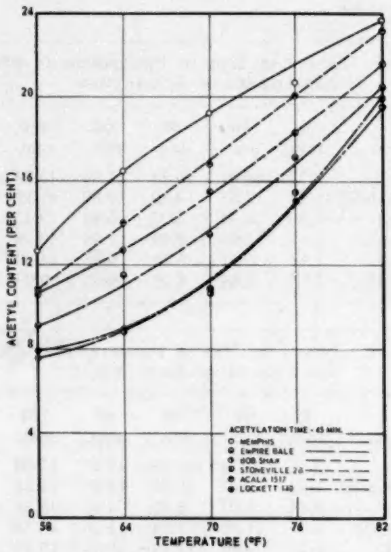

FIG. 7. *The change in acetyl content with acetylation temperature using a 10-min., 170°F presoak.*

sults with the acetyl values obtained for 240 min. at 70°F is shown below. At the end of 18 hrs. at 70°F the acetyl content of the fibers were still slightly below the maximum obtained at the higher presoaking temperatures.

The hot glacial acetic apparently enlarges the capillaries of the fibers at a greater rate, and the saturation is reached much sooner, thus, permitting a more rapid diffusion of the acetylating mixture into the inner parts of the fiber. The higher the temperature the faster the saturation point is reached.

The different varieties of cotton reacted at different rates to the effect of the temperature of presoaking. The most immature fiber, Memphis, reached its maximum acetylation in 10 min. at the three higher presoaking temperatures, while the more mature fibers, Bob Shaw and Lockett 140, took a con-

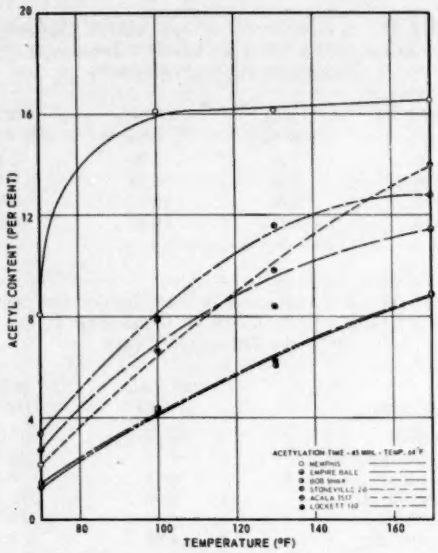

FIG. 8. *The change in acetyl content with presoaking temperature using a 10-min. presoaking period.*

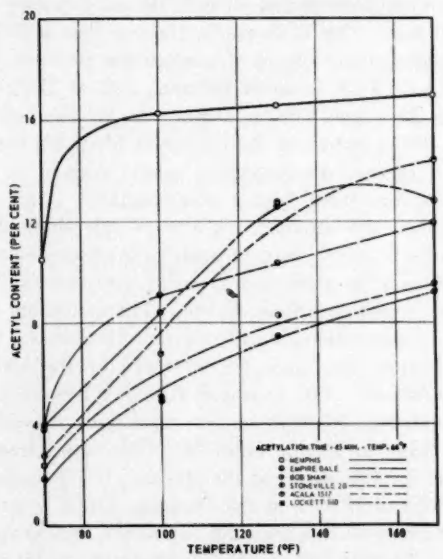

FIG. 9. *The change in acetyl content with presoaking temperature using a 30-min. presoaking period.*

siderably longer time—*i.e.,* 30 min. at 170°F, 60 min. at 130°F, and 120 min. at 100°F—to reach maximum acetylation. Generally speaking the more mature the fiber, the less the degree of acetylation under constant conditions. This may be shown by

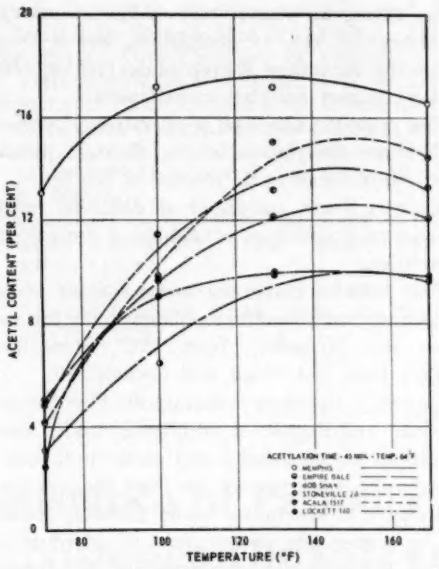

FIG. 10. *The change in acetyl content with presoaking temperature using a 60-min. presoaking period.*

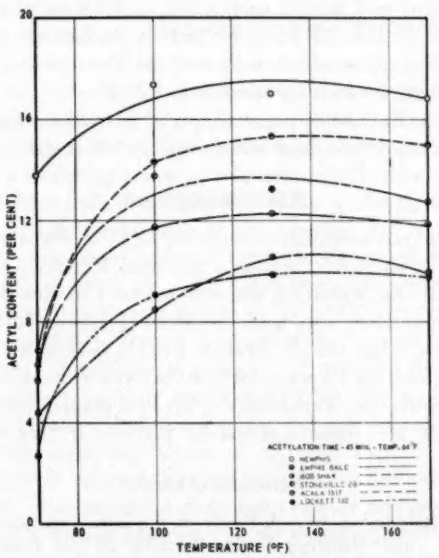

FIG. 11. *The change in acetyl content with presoaking temperature using a 120-min. presoaking period.*

comparison of the acetyl content in Tables IV–VII with the maturity values shown in Table I. The order of increasing maturity is (*1*) Memphis, (*2*) Empire Bale 92, (*3*) Stoneville 2B, (*4*) Acala 1517, (*5*) Bob Shaw, and (*6*) Lockett 140, while the order

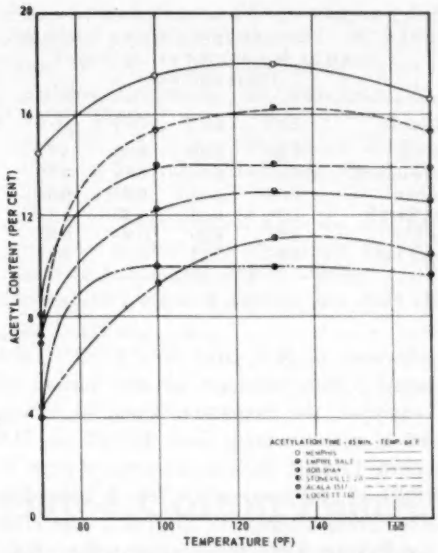

FIG. 12. *The change in acetyl content with presoaking temperature using a 240-min. presoaking period.*

of decreasing acetyl content is (*1*) Memphis, (*2*) Acala 1517, (*3*) Stoneville 2B, (*4*) Empire Bale 92, (*5*) Bob Shaw, and (*6*) Lockett 140. Thus, with the exception of Empire Bale 92 and Acala 1517, whose order is reversed, the more mature the fiber the less the acetyl content.

The higher degree of acetylation of the immature fibers is due in part to the greater percentage of amorphous structure and lesser percentage of crystallinity. The immature fibers exhibit greater swelling due to the collapse of the thin fiber walls and, thus, allowing greater diffusion of the acetylating mixture. Other factors such as gum and wax content, mineral content, alpha cellulose, etc., may also effect the degree of acetylation.

A comparison of the Micronaire readings in Table I with the acetyl content shows that generally the higher the Micronaire reading the lower the acetyl content of the cotton. This is to be expected as the more mature the cotton the thicker the fiber walls and, thus, the higher the Micronaire reading. Both the fiber fineness and the maturity affect the degree of acetylation, and both factors have to be taken into consideration in determining which cotton would be expected to exhibit the highest acetyl content.

The effect of the temperature of acetylation on the degree of acetylation is described in part *II* of this study. The results of these determinations are shown in Table VIII and Figure 7.

TABLE IX. PRESSLEY INDEX (FIBER STRENGTH) OF SAMPLES ACETYLATED AT DIFFERENT TEMPERATURES

Cotton	58°F	64°F	70°F	76°F	82°F*
Memphis	6.02	6.89	6.09	5.52	—
Empire Bale 92	6.62	6.91	6.49	6.16	—
Bob Shaw	7.70	6.68	6.84	6.33	—
Stoneville 2B	7.16	6.64	6.80	6.17	—
Acala 1517	8.01	8.29	6.93	6.83	—
Lockett 140	6.53	7.25	6.27	6.01	—

* The fibers were too weak to obtain a satisfactory break.

An increase of 24°F from 58°F to 82°F, doubled the acetyl values obtained for the various fibers. For example, the immature Memphis cotton increased in acetyl content from 12.69% to 23.68%, the mature Lockett 140 cotton increased from 7.96% to 19.88% and an intermediate cotton, Stoneville 2B, increased from 10.68% to 21.51%. The effect of the temperature of acetylation was determined in six-degree increments, and the differences in acetyl content between increments were found to be relativley constant. The fiber degradation increased noticeably with each increase in temperature as shown in Table IX. At 82°F the degradation to the cotton fibers was so great that the tensile strength of the fibers could not be determined.

It was also found that as the acetyl values increased the moisture content decreased and the fiber fineness decreased (Micronaire readings increased). The fiber strength generally decreased with increasing acetyl content and increasing time of presoaking. The tensile strength per unit weight of cellulose, however, probably experiences little change except possibly in the 76°F and 82°F acetylations as the fiber weight increases approximately 25% at the monoacetate stage.

The dye test for evenness of acetylation produced uniform coloring throughout the cotton samples and, thus, showed that the acetylation was even throughout the cotton fibers.

Conclusions

An increase in the temperature of the glacial acetic acid used for presoaking increases the rate in which maximum acetylation is reached under constant acetylation conditions.

Higher degrees of acetylation are obtained at the higher presoaking temperatures for short periods, 10 to 60 min., of presoaking.

Increasing the temperature of the presoaking acid increases the rate of acetylation, but it does not effect the maximum degree of acetylation obtained under constant acetylation conditions.

The optimum time and temperature of presoaking (maximum acetylation in the shortest presoaking time) were found to be 10 min. at 170°F.

Various fibers acetylated at different rates and degrees under constant conditions of presoaking and acetylation.

The order of maximum acetyl content under the same acetylating conditions obtained for the various fibers was Memphis, Acala 1517, Stoneville 2B, Empire Bale, Bob Shaw, and Lockett 140.

Generally, the more immature the fiber the greater the rate and degree of acetylation under constant conditions of presoaking and acetylation, and conversely, the more mature the fiber the less the rate and degree of acetylation under constant conditions.

The higher the temperature of acetylation, the greater the degree of acetylation and the greater the degradation of the cotton fibers.

In general, under the same conditions of presoaking and time of acetylation, an increase of 24°F, from 58°F to 82°F, approximately doubled the acetyl content obtained but weakened the fibers so that fiber strengths were unobtainable at 82° F.

The method of presoaking and acetylation used in this study produced evenly acetylated cotton fibers.

Acknowledgment

Acknowledgment is made to the U. S. Department of Agriculture's Southern Regional Research Laboratory for supplying the cottons used in this study. The authors also wish to acknowledge the aid received from the A. French Textile School and the Engineering Experiment Station, both at the Georgia Institute of Technology. We especially wish to thank Mr. Alton Colcord for his help in this work.

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Resistance of Partially Acetylated Cotton Fabric to Nitrogen Dioxide and to Hydrogen Chloride

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IN an investigation of the properties of partially acetylated cotton fabric it was observed that this chemically modified cotton was much more resistant to the tendering action of nitrogen dioxide than ordinary bleached cotton fabric. This property is of special interest because of the possible use of partially acetylated cotton filters for removing dusts from fume laden air or for other purposes where resistance to oxidizing agents or to acids is required. The purpose of the work reported in this paper was to study the effects of mixtures of nitrogen dioxide and air on partially acetylated cotton and on ordinary bleached cotton. For the purpose of comparing the oxidizing action of nitrogen dioxide with hydrolytic effects, data were also obtained on the action of mixtures of hydrogen chloride and air, because hydrogen chloride has no oxidizing action on cotton but hydrolyzes the glycosidic linkages of the cellulose. The changes which were caused by exposure of the fabrics to these gases were measured by determinations of the breaking strength, fluidity in cuprammonium solution, carboxyl content, and copper number.

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Experimental

Materials

Two fabrics were used, one an 80 × 80 bleached cotton print cloth which weighed 3.3 oz./sq.yd. and the other a portion of the same fabric after it had been partially acetylated [3] to an acetyl content of 21%. The partially acetylated fabric weighed 3.9 oz./sq.yd. Breaking strengths of the two fabrics were 48.3 lbs. and 46.8 lbs., respectively.

The nitrogen dioxide was obtained from a commercial cylinder of this gas, which was stated by the manufacturer to have a purity of 98%. It is well known that nitrogen dioxide, under ordinary conditions, is an equilibrium mixture of nitrogen dioxide and nitrogen tetraoxide. The hydrogen chloride was obtained from a commercial cylinder of anhydrous gas stated to have a purity of 99%. Laboratory air having a controlled relative humidity of 45% to 50% at a temperature of 76° to 78°F was used to dilute the gases.

Methods

Samples of the fabrics, bleached cotton and partially acetylated cotton, were exposed to mixtures of nitrogen dioxide and air, or to hydrogen chloride and air, in a 9.3 l. desiccator. Two 8 in. × 10 in. samples of each fabric were used in each exposure after they had been conditioned in the air of the laboratory. The exposure operation consisted in partially evacuating the desiccator containing the two samples, introducing a measured volume of either nitrogen dioxide or hydrogen chloride, and then admitting air from the laboratory until atmospheric pressure was reached. The samples were allowed to remain in the desiccator for 6 hrs. after which they were washed thoroughly in tap-water and air dried.

Breaking strength was determined by the raveled strip method [1]; carboxyl content by the calcium acetate method [4]; copper number by a modification of the Braidy method [4]; and fluidity by the cuprammonium method [2].

In Figures 1, 2, 3, and 4 each point on the curves represents the average obtained from a minimum of two replicate samples. At least ten breaking strength determinations were made on each sample.

Results

The data summarized in Figure 1 show that the partially acetylated cotton retained most of its breaking strength after exposure to nitrogen dioxide. Good strength retention was also shown by partially acetylated cotton after exposure to hydrogen chloride, but the various concentrations of hydrogen chloride caused significantly greater strength losses than nitrogen dioxide. Ordinary bleached cotton showed large strength losses when exposed to either gas. It may be concluded that the partial acetylation of cotton greatly increases its resistance to the tendering action of either nitrogen dioxide or hydrogen chloride.

The data summarized in Figure 2 show that partially acetylated cotton does not increase in cuprammonium fluidity as much as ordinary bleached cotton when exposed to either nitrogen dioxide or hydrogen chloride. These results are in agreement with the breaking strength data discussed above.

The data summarized in Figure 3 show that partially acetylated cotton shows little increase in carboxyl content after exposure to nitrogen dioxide, while ordinary bleached cotton shows a very large increase. On the other hand, hydrogen chloride has

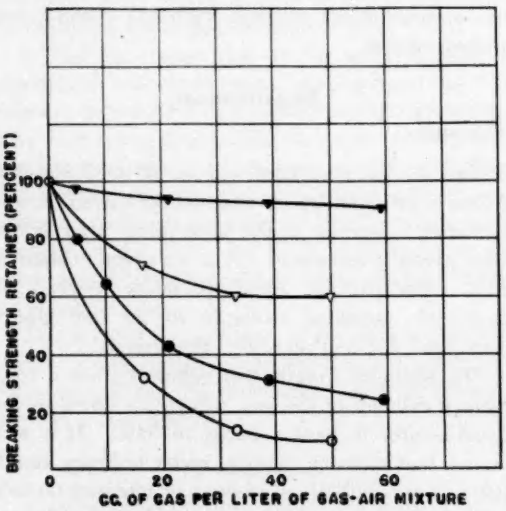

FIG. 1. *The effect of NO_2 and HCl on the breaking strength of partially acetylated cotton fabric as compared with ordinary bleached cotton fabric. Samples exposed for 6 hrs.* ●, *ordinary bleached cotton exposed to NO_2;* ▼, *partially acetylated cotton exposed to NO_2;* ○, *ordinary bleached cotton exposed to HCl;* ▽, *partially acetylated cotton exposed to HCl.*

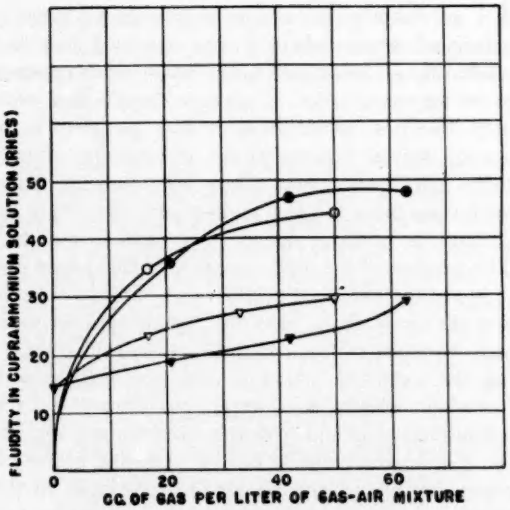

FIG. 2. *The effect of NO_2 and HCl on the fluidity in cuprammonium solution of partially acetylated cotton fabric in comparison with ordinary bleached cotton fabric. Samples exposed for 6 hrs.* ●, *ordinary bleached cotton exposed to NO_2;* ▼, *partially acetylated cotton exposed to NO_2;* ○, *ordinary bleached cotton exposed to HCl;* ▽, *partially acetylated cotton exposed to HCl.*

essentially no effect on the carboxyl content of either of the cottons. This is as expected because hydrogen chloride has no oxidizing action while nitrogen dioxide is known to oxidize the primary hydroxyl groups of cellulose to produce carboxyl groups.

The data summarized in Figure 4 show that the copper number was not greatly increased when partially acetylated cotton was exposed to either nitrogen dioxide or to hydrogen chloride while large increases were observed in the bleached cotton. The very large increases in copper number, when the ordinary cotton was exposed to nitrogen dioxide, are in agreement with its action as an oxidizing as well as a hydrolyzing agent, because either oxidation or hydrolysis of cellulose is known to produce aldehydic reducing groups.

Discussion

The experiments described above show that partially acetylated cotton is much more resistant to the action of nitrogen dioxide or hydrogen chloride than ordinary bleached cotton. This is shown by experiments involving breaking strength, cuprammonium fluidity, carboxyl content, and copper number. A possible explanation of the protective effect of partial acetylation is that by substituting acetyl groups for the more accessible of the hydroxyl groups, these larger groups interfere with access of the gas to vulnerable groupings in the cellulose molecule. It is known that nitrogen dioxide oxidizes preferentially the primary hydroxyl groups of cellulose [6, 7], although oxidation of other hydroxyl groups may occur to some extent [5]. Acetylation protects the primary groups against oxidation, as shown by the lack of a significant increase in carboxyl groups when partially acetylated cotton is exposed to nitrogen dioxide. However, this protection of the primary groups does not explain the resistance of partially acetylated cotton to loss of strength and increase in cuprammonium fluidity when exposed to nitrogen dioxide because oxidation limited to the primary hydroxyl groups would not break the cellulose chain. The protective action of acetylation against breaking of the cellulose chains is probably due to blocking of hydrolysis of the glycosidic linkages. Nitrogen dioxide appears to act on cellulose as a hydrolyzing as well as an oxidizing agent, since it decreases the breaking strength and increases the fluidity of ordinarily bleached cotton. The protective action of acetylation against hydrolysis is shown by the re-

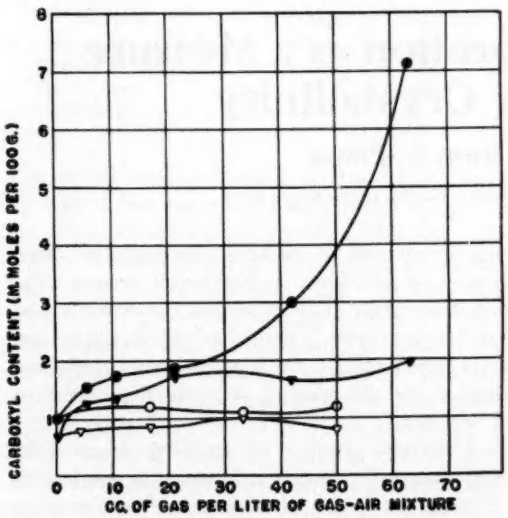

FIG. 3. *Effect of NO_2 and HCl on the carboxyl content of partially acetylated cotton in comparison with ordinary bleached cotton. Samples exposed for 6 hrs. ●, ordinary bleached cotton exposed to NO_2; ▼, partially acetylated cotton exposed to NO_2; ○, ordinary bleached cotton exposed to HCl; ▽, partially acetylated cotton exposed to HCl.*

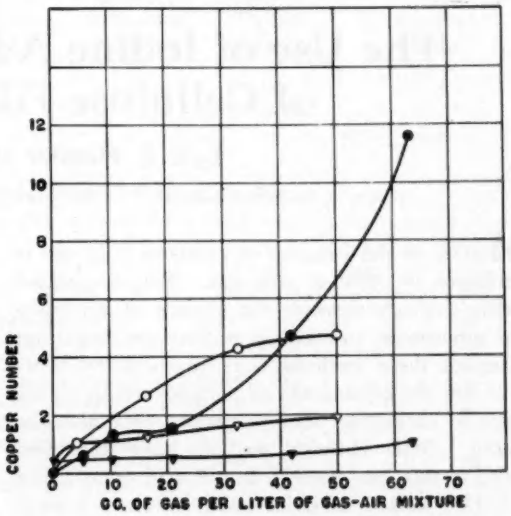

FIG. 4. *Effect of NO_2 and HCl on the copper number of partially acetylated cotton in comparison with ordinary cotton. Samples exposed for 6 hrs. ●, ordinary bleached cotton exposed to NO_2; ▼, partially acetylated cotton exposed to NO_2; ○, ordinary bleached cotton exposed to HCl; ▽, partially acetylated cotton exposed to HCl.*

sistance of partially acetylated cotton to hydrogen chloride, a reagent which is known to degrade cellulose by hydrolysis of the glycosidic linkages, but which has no oxidizing action.

Summary

Exposure of partially acetylated cotton to nitrogen dioxide and air mixtures, and to hydrogen chloride and air mixtures, showed that this chemically modified cotton is resistant to the action of these gases as compared to ordinary bleached cotton. This was shown by data on breaking strength, cuprammonium fluidity, carboxyl content, and copper number. A possible explanation for the resistance of partially acetylated cotton to oxidation and hydrolysis is discussed.

Acknowledgments

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The Use of Iodine Adsorption as a Measure of Cellulose Fiber Crystallinity

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MUCH of the behavior of cellulose fiber can be attributed to cellulose structure. For this reason, methods which measure the amount of crystalline and amorphous material in a fiber are important. Many of these methods were reviewed by Ward [19], and the crystallinity of cellulose and its significance in evaluating fiber properties were also discussed. Other chemical methods have since been added to this list—namely, formic acid esterification [13, 17], reaction of sodium with cellulose in liquid ammonia to give trisodium cellulose [18], and oxidation with chromic oxide. [3].

The iodine adsorption of cellulose received extensive study by Schwertassek [15] as early as 1931 as a tool for research in studying mercerization. More recently, he published a number of papers using iodine adsorption [15] in studies on cellulose fiber crystallinity. From standpoints of simplicity and ease of determination, the method merits study as a technique for determining cellulose fiber structure and behavior.

In a research program for studying means of detecting changes in the cotton fiber due to overheating in ginning, the iodine adsorption method was given a thorough trial. This led to a number of cotton problems relating to heating, kier-boiling, breeding, and agronomy.

Procedure

Raw cotton was used in most of the tests, largely because it was found that pretreatment has very little

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TABLE I. CRYSTALLINITY OF CELLULOSE FIBER AS MEASURED BY IODINE ADSORPTION

Sample	No. of tests	Treatment	Iodine (mg./g. of sample)	Crystallinity (%)
Acala cotton	17	none	47	89
Acala cotton	14	dewaxed	36	91
Acala cotton	4	kier-boiled	44	89
Acala cotton	10	mercerized	147	64
Viscose rayon	18	none	227	45
Acetate rayon*	2	none	349	15
Wood pulp	2	none	136	67
Wood pulp	2	none	200	51

* Cellulose derivative.

effect on the iodine adsorption value. Severe grinding may break up the crystallites, as is the case when the vibrating ball mill is used on cellulose fibers [6]. Clipping the samples with scissors was found to facilitate handling, although this is not essential. Dewaxing and kier-boiling has little effect on iodine adsorption, as shown in Tables I and VI.

The method used is essentially that of Schwertassek [15], with a few minor modifications. A sample of 0.3 g. of cotton was treated with 2 cc. of iodine solution (5 g. of iodine and 40 g. of potassium iodide dissolved in 50 cc. of distilled water) in a 250-cc. beaker. After the cotton and solution were thoroughly mixed, 100 cc. of a saturated solution of sodium sulfate was measured accurately into the beaker. The beaker and contents were then stored in a dark place for 1 hr. The iodine remaining in solution was determined by titrating 50 cc. with $N/50$ sodium thiosulfate to which had been added 50 cc. of distilled water and 1 cc. of starch solution (1 g. of starch per 100 cc. of water). A blank on the original iodine solution before adsorption was determined at the same time in a like manner. Calculations were made as follows:

$$\frac{(a - b) \times 2.04 \times 2.54}{.3} = \frac{\text{mg. } I_2}{\text{g. sample}},$$

where a = volume (cc.) of $N/50$ thiosulfate solution required for blank, and b = volume (cc.) of $N/50$ thiosulfate solution required for determination.

A ratio of the milligrams of I_2 adsorbed per gram of cellulose to 412 (the milligrams of I_2 adsorbed per gram of methocel) gave a value for the amorphous fraction. Crystallinity was obtained by subtracting % amorphous fraction from 100.

Maturity values were obtained by using a polarizing microscope.

Results

Some values for the crystallinity of cellulose fibers are shown in Table I. The values for Acala cotton show that pretreatment such as dewaxing and kier-boiling do not affect the results appreciably. The crystallinity range was from 15% to 91%, based on a water-soluble sample of methocel which had the highest iodine adsorption of any cellulose material determined.

TABLE II. CELLULOSE CRYSTALLINITY (%) DETERMINED BY VARIOUS METHODS

Material	HCl-$FeCl_3$ hydrolysis (Phillip)	HCl-$FeCl_3$ hydrolysis (Howsmon)	X-ray (Hermans)	Formic acid esterification (Nickerson)	Heavy water (Frillette)	Iodine adsorption
Cotton	86	86	70	84	75–82	83–91
Mercerized cotton	73	70		72		64–71
Viscose rayon	68	45	40	46	44	45
Wood pulp		81	65		36–64	51–77

TABLE III. EFFECT OF HEAT ON COTTON CELLULOSE

Sample	Treatment	Iodine (mg./g. of sample)	Crystallinity (%)
Acala raw cotton	none	45	89
Acala raw cotton	200°F, 1 hr.	51	88
Acala raw cotton	300°F, 1 hr.	55	87
Acala raw cotton	350°F, 1 hr.	62	85
Acala raw cotton	400°F, 1 hr.	70	83
Acala raw cotton	550°F, 1 hr.	147	64
Acala raw cotton, dry	250°F, 4 hrs.	58	86
Acala raw cotton, 8% H_2O	250°F, 4 hrs.	56	86
Acala raw cotton, wet	250°F, 4 hrs.	58	86
Acala raw cotton, dry	250°F, 20 hrs.	56	86
Acala raw cotton, 8% H_2O	250°F, 20 hrs.	54	87
Acala raw cotton, wet	250°F, 20 hrs.	56	86

Crystallinity values of 15% for cellulose acetate and 45% for viscose were among the lowest values obtained. Wood pulp crystallinity varied from 51% to 67%, which are well within the range of 36% to 81% determined by other methods (see Table II).

A comparison of the iodine adsorption method with physical and chemical methods for crystallinity is shown in Table II. The iodine adsorption method compares favorably with other chemical methods as to range of crystallinity, and gives somewhat higher values than the physical methods reported here and in the literature.

The original purpose of exploratory work with the iodine adsorption method was to find whether the heat used in gin-drying is sufficient to open the crystallites enough so that differences can be determined by the method. Table III shows the results of heating cotton at various temperatures and for various periods of time. Heating cotton for 1 hr. from 200° to 550°F showed a progressive opening of the crystallites, as measured by iodine adsorption. The big drop came at 550°F, with a decrease in crystallinity of 25% from that of the original raw cotton. This sample had turned brown and showed some evidence of charring. The other treatments in Table III were for the purpose of finding whether preconditioning of the cotton with regard to moisture has any effect on iodine adsorption. Samples were heated for 4 and 20 hrs. at 250°F with the cotton dry, containing 8% moisture, and wet. One of the present authors [7] found that the more moisture in the sample prior to drying, the greater the cellulose degradation, as measured by viscosity. Apparently, preconditioning of the cotton with reference to moisture does not play a part in decreasing crystallinity.

A number of workers reported the increased crystallinity of cellulose material in contact with strong acids. In fact, this has been one of the criticisms of the HCl hydrolysis method using $FeCl_3$ as a catalyst [2, 11]. There now seems to be definite information that strong acids build up the amorphous phase into a crystalline phase in cellulose fiber. By using 6*N* HCl at room temperature, an increase in crystallinity occurs with time, as shown in Table IV. A solution of 75% ethylene glycol and 25% monoethanolamine proved to be an excellent means of purifying cellulose without noticeably changing the cellulose molecule [8]. A 1-hr. boil with this solution did not significantly change the crystallinity, even though this treatment gave cellulose of high purity. By dissolving this sample and reprecipitating it in water, a drop in crystallinity from 83% to 73% was effected.

Dry-land and irrigated cotton were studied, and the results are given in Table V. Ten different varieties grown under nearly identical conditions except for water gave a crystallinity value of 86% for the dry-land cotton and 81% for the irrigated cotton. The dry-land cotton had a greater maturity, which may account for this small difference.

The results in Tables VI, VII, and VIII show that the degree of crystallinity is a function of fiber development and maturity. The samples of Table VI show a wide range of maturity and decreasing order of crystallinity as the maturity diminishes. Since cotton of low maturity has more extraneous materials other than cellulose, a kier-boil of 1 hr. with 2% NaOH was used to find out if the lower crystallinity was due to materials other than cellulose. The results indicate that kiering has very little effect on the crystallinity.

Table VII reports cottons developed at various periods of growth. Here again, maturity, or cell-wall development, has an effect on the values for the crystalline fraction. The low crystallinity value of 82% is for cotton which was highly underdeveloped because the bolls were not opened normally. The

TABLE IV. EFFECT OF CHEMICAL REAGENTS ON COTTON CELLULOSE CRYSTALLINITY

Sample	Treatment	Iodine (mg./g. of sample)	Crystallinity (%)
Acala raw cotton	none	49	88
Acala raw cotton	3 hrs., 6*N* HCl, 70°F	44	89
Acala raw cotton	18 hrs., 6*N* HCl, 70°F	36	91
Acala raw cotton	66 hrs., 6*N* HCl, 70°F	34	92
Macha raw cotton	none	70	83
Macha raw cotton	boiled 1 hr., 75% ethylene glycol, 25% monoethanolamine	65	84
Macha raw cotton	dissolved in copper ethylenediamine, reprecipitated	112	73

TABLE V. EFFECT OF IRRIGATION *vs.* DRY-LAND ON COTTON CELLULOSE CRYSTALLINITY

Method of watering	No. of tests	Maturity (%)	Iodine (mg./g. of sample	Crystallinity (%)
Dry-land*	20	83	57	86
Irrigated*	20	73	77	81

* 10 varieties.

date 9/6 was that for a thin-walled sample which was opened normally.

Generally speaking, long cottons are finer than short cottons, and, as a consequence, may show less maturity, as based on cell-wall thickness. The first four samples reported in Table VIII were of the same order of maturity and showed a high degree of crystallinity. The longest cotton had the lowest maturity and the lowest crystallinity. In cases where maturity was known, the correlation of low maturity with low crystallinity has been striking.

Discussion

The use of methocel as an example of a completely amorphous cellulose may be open to some criticism. However, the values for crystallinity obtained by chemical methods (Table II) are in good agreement with the values obtained by iodine adsorption. Differences in samples may account for some of this variation. For example, this work has shown that the development of the cotton plays a part in the ultimate crystallinity. Mercerization is not well controlled, and therefore variations are to be expected. The amount of opening of the crystallites depends upon the concentration of NaOH, the tension, the time, and the temperature of the process. Viscose rayon crystallinity undoubtedly depends upon the previous history of the starting product. Wood pulp crystallinity is a function of the starting material, the type of pulping, and the length of cook. Therefore, very close agreement cannot be expected in basic cellulose crystallinity.

TABLE VI. EFFECT OF MATURITY ON COTTON CELLULOSE CRYSTALLINITY

Sample	Maturity (%)	Iodine (mg./g. of sample)	Crystallinity (%)
Raw cotton	96	50	88
Raw cotton	78	75	82
Raw cotton	50	80	81
Raw cotton, kier-boiled	50	78	81

TABLE VII. EFFECT OF BLOOMING DATE ON COTTON CELLULOSE CRYSTALLINITY

Date of blooming	Maturity (%)	Micronaire fineness	Iodine (mg./g. of sample)	Crystallinity (%)
7/25	84	3.9	49	88
8/16	87	4.8	38	91
9/6	45	2.3	64	84
Immature at frost	52	2.4	73	82

TABLE VIII. EFFECT OF LENGTH OF FIBER ON COTTON CELLULOSE CRYSTALLINITY

Staple	Maturity (%)	Micronaire fineness	Iodine (mg./g. of sample)	Crystallinity (%)
$\frac{3}{4}$ in.	87	5.0	36	91
$\frac{15}{16}$ in.	90	5.1	40	90
1 in.	88	4.9	38	91
$1\frac{3}{32}$ in.	82	4.7	42	90
$1\frac{9}{32}$ in.	72	3.9	74	82

The milligrams of iodine adsorbed per gram of sample ranging from 36 to 349 (Table I) for from 15% to 91% cellulose crystallinity indicate a high degree of sensitivity for the iodine adsorption method. Crystallite size may enter into the determination of crystallinity when the origin of the cellulose is different. The crystalline structure of the cellulose molecule indicates that the microfibrillae vary in size, depending upon whether the cellulose fiber came from cotton, a bast fiber, wood, or some other source. In the case of cotton fiber, no evidence is available which proves that crystallite size is a function of fiber development. The data on crystallinity using the iodine adsorption method on cotton fiber of low maturity may indicate that smaller crystallites give greater surface area for adsorption and, consequently, lower crystallinity.

For a number of years, x-ray has been used as the criterion of crystallinity measurements. Generally speaking, the amount of crystalline material in a cellulose fiber is lower by this method of measurement. X-ray measures the crystalline fraction, whereas the chemical methods measure the accessible or amorphous fraction of cellulose. Ranby [14] tried to reconcile some of these differences by a better understanding of the cellulose molecule. Cotton cellulose with a micellar width of 90 Å. has 20%–25% of the cellulose chains on the surface of the filaments, and to a depth of 5 Å. Under these conditions, it is not difficult to understand why the chemical and x-ray methods do not agree very closely. Sisson [16] pointed out that there are regions in the cellulose molecule which are not sufficiently close to give a crystalline lattice, and these regions may be interpreted to be amorphous, although in reality they are crystalline. More recently, Meyer [12] stated that attempts to estimate the ratio of crystalline to amorphous material in partially crystallized cellulose fibers by comparing

of the intensity of suitable spots and diffuse maxima is with the assumption that if it were possible to eliminate the amorphous portion, no radiation would be scattered towards regions outside the spots. He further stated that this assumption is not justified, if only because of inevitable incoherent radiation. Also, the intensity of diffraction waves from crystalline and amorphous material cannot be added. Therefore, for these and other reasons, he believed that the results obtained are useful only for the purpose of verifying the increase or decrease of crystallinity in a given fiber as a result of processing, and should not be considered as indicating the ratio of crystalline to amorphous material. The fact that the crystallinity values of cotton determined by x-ray are invariably around 70% indicates that the method lacks sensitivity. A variety of cotton grown under different environmental conditions produces fiber of varying wall thickness, degree of polymerization, and spiral structure [9]. It is inconceivable that a cotton plant which can develop fiber of widely different character, as measured by differences in physical properties, can show no fiber structural differences based on crystallinity. The data presented by the iodine adsorption method show that cotton cellulose of lower maturity has fewer orderly regions in the cellulose molecule. Since kiering and treatment with reagents for removing materials other than cellulose have no significant effect in changing the crystallinity of underdeveloped cotton, the lower crystallinity values for low-maturity cotton can hardly be attributed to extraneous materials.

By means of differential dyeing, Goldthwait [4] demonstrated a structural difference in the cellulose from thin-walled, or immature, cotton and cotton having thick walls, or being fully matured. Since the green dye has a slower dyeing rate and its molecules are twice as large as those of the red dye [5], the reason the immature fiber dyes green would seem to be greater accessibility or lower crystallinity. The fact that fiber taken from immature bolls and dyed before crystallization takes place [1] dyes green is additional evidence that the immature fibers are of a lower crystallinity order, as measured by the iodine adsorption method.

The hydrolysis method using HCl and a catalyst for determining crystallinity has been shown to increase crystallinity [2, 11]. Table IV shows an increase of crystallinity with time when strong HCl is allowed to act on cotton fiber. There is, of course, the possibility that this increase is due to short-chain cellulose molecules in the amorphous regions dissolving. The crystallinity values of Howsmon [11] in Table II were corrected for the recrystallization of cellulose, and are in very close agreement with the iodine adsorption results for three out of four materials determined. The higher value for wood pulp may have been due to a mild pulping process.

Table III shows the effect of heat on the crystallinity of cotton fiber. Apparently, considerable heat is necesary to open up the crystallites of cotton cellulose, and only in severe heating will the iodine adsorption method show substantial crystallinity change. Heat applied with varying amounts of moisture did not show any change in the amount of iodine adsorbed, even for 20 hrs.

Some evidence is available that surface heat is more effective in opening the crystallite than hot air. Cotton rotated against a hot surface for a few minutes showed a drop in crystallinity of from 89% to 79%. Data on this phase of the effect of heat were not used because of the difficulty of having any control which could reproduce the results; however, the indications are that surface heat may be more destructive to cotton than hot air when used to dry cotton in the gin.

The results in Table V are for cotton which was under stress for moisture and cotton which was irrigated to give better than a bale to the acre. Except for water, the conditions of the experiment were as nearly alike as it was possible to make them. Under drought conditions, cotton has a tendency to mature early and be somewhat thinner walled. Irrigation forces growth to the end of the season, and the tendency is toward immaturity [10]. In this experiment the irrigated cotton was 10% less mature and the crystallinity was 5% lower, which may or may not be significant; nevertheless, the finding that lower maturity gives lower crystallinity is supported. Table VI shows that as maturity decreases, crystallinity decreases, and kier-boiling has little effect. Table VII, based on blooming date data, substantiates this evidence. As the bolls develop and the season progresses in maturing cotton, the length of time to develop the fiber to full maturity becomes progressively longer. Late-developed cotton shows decreased fineness, strength, and length. The fiber is lower in maturity, and wall thickness decreases. From this evidence it is shown that development slows down as the season progresses, and the length of time to develop the cotton fully may in some cases be almost again as long as for the early-season cot-

ton. Apparently, this lack of development as the season progresses is reflected in cellulose structure, since the data show lower crystalline structure.

The difference in the physical behavior of cotton of various lengths prompted the crystallinity determination of cottons of $\frac{3}{4}$ in. to more than $1\frac{1}{4}$ in. In general, shorter cottons have greater wall thickness when developed under normal conditions. The reason for this is that a short fiber will develop faster and reach a greater wall thickness. Variety and environment can influence this kind of development; however, the fineness figures in Table VIII show this to be true for cottons of five different lengths. Here again, the values for crystallinity seem to have been influenced more by fiber development than by length. The coarser fibers all have high crystallinity values, regardless of length.

Summary

The iodine adsorption method has been found useful in detecting changes in cotton cellulose structure (crystallinity) brought about by heat and chemical action. For the first time, it has been possible to demonstrate cellulose crystallinity differences due to fiber development, as measured by fiber fineness and maturity. Cotton fiber in lengths from $\frac{3}{4}$ to $1\frac{9}{32}$ in. did not show crystallinity variations when maturity was of the same magnitude. Comparison of the results obtained by this method with those of other chemical methods for determining crystallinity show good agreement, considering differences which may have resulted from the source of cellulose material.

Acknowledgment

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CORRECTION

On page 585 of the June, 1954, issue of TEXTILE RESEARCH JOURNAL, in an article entitled "Some Observations on European Cotton Research," reference was made to the "Nylon Spinners' Research Association." This reference should have been to the "British Nylon Spinners, Ltd.," manufacturers of nylon yarns and staple fiber in the United Kingdom. The laboratories for research and development maintained by this company form no part of any research association. We are grateful to Mr. R. M. Lodge, research manager of the above organization, for calling our attention to this error.

HELMUT WAKEHAM

Modification of Wool by the Application of Linear Synthetic Polyamides

Part V: Pretreatment with Ethanolic Potassium Hydroxide*

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Abstract

Ethanolic potassium hydroxide solutions in concentrations from 0.1% to 5.0% have been used to pretreat wool effectively for the application of *N*-alkoxymethyl polyamides to prevent felting shrinkage. The alcoholic alkali may be used purely as a pretreatment, or the alkali can be incorporated in the alcoholic resin solution. Even when the alkali pretreatment does not in itself reduce the felting shrinkage, effective shrinkproofing is obtained with less than 1% resin based on the weight of wool.

IT has been shown [2] that when modified nylon resins containing alkoxy- and/or hydroxymethyl groups are used to prevent the felting shrinkage of wool, optimum results are obtained only when either the wool is rigorously cleaned—*e.g.*, by ethanol extraction—or the fiber surface is modified by a reagent such as hydrogen peroxide. Other reagents capable of modifying the wool fiber surface may also be used to pretreat the wool.

The present paper is concerned with the use of alcoholic potassium hydroxide as a pretreatment.

Materials and Methods

N-Ethoxymethyl Nylon

The resin contained 8.8% total formaldehyde, and was supplied by Imperial Chemical Industries Limited, Melbourne, Victoria, Australia.

The shrinkproofing properties of this product are identical to those of the *N*-methoxymethyl nylon used previously [1]. However, it is more readily soluble in alcohol than the *N*-methoxymethyl nylon. A 5% solution of *N*-ethoxymethyl nylon in 75% ethanol will keep indefinitely without gelling.

Wool

A commercially scoured fabric of the following construction was used: weave, plain; warp yarn, 2/30's worsted; weft yarn, 2/30's worsted; ends/in., 27; picks/in., 20; weight, 3.4 oz./sq.yd.

Felting Shrinkage

All tests were carried out in a washing machine of the horizontal cylindrical rotating-cage type, using 0.05% soap solution at 37°–40°C. Up to forty 6-in. squares of fabric were washed simultaneously, area shrinkage being measured as described previously [1]. Washing was continued until the untreated control samples had shrunk 40% in area.

Method of Application of Resin

The method of applying the polymer previously described [1]—steeping the fabrics in a resin solution in ethanol and then mangling to remove excess solution—has disadvantages. Firstly, the solution soon becomes contaminated with impurities from the wool and has to be discarded, thus necessitating recovery and purification of the resin. Secondly, since the viscosity of the solution varies with both temperature and time of standing, it is difficult to apply a specific amount of resin with any certainty.

Two other methods of application were therefore adopted. Both have been used quite successfully on the pilot scale.

(*1*) The wool is placed in a container, which is slowly rotated while the required amount of resin solution is sprayed or poured on the goods. To get an even deposit of resin, it is necessary to have a

* Parts I–IV appeared in the March, 1951, September, 1951, September, 1953, and July, 1954, issues, respectively.

liquor:goods ratio of at least 2:1. After the goods are tumbled for a short time, the alcohol is evaporated with a current of cool air. When the liquor remaining in the goods has dropped to 20%–30%, the resin is hydrolyzed to nylon by immersing the wool in 2*N* aqueous hydrochloric acid at 25°C for ½–¾ hr., as described previously [1].

(*2*) The required amount of resin solution is placed in a container, and the wool is pressed into the solution until it is just covered. With the single fabric squares, this is done in a tall 50-ml. beaker fitted with a plunger made from polythene rod. A small screw-press capable of taking six separate samples is used to supply the necessary pressure. On the pilot scale an hydraulic press is used, which permits liquor:goods ratios as low as 1:1 to be used. The material is left in the press for a short time, and then removed and tumbled in a rotating container for about 5 min. to ensure that the resin deposit is even. The wool is then dried, and the resin is hydrolyzed as above. With single pieces of fabric, the tumbling step is omitted and the wool is dried by spreading it out on a sheet of glass and blowing air over it.

The latter method, unless otherwise stated, was used throughout this work to apply the resin. Method (*1*) is suitable only for large-scale treatments. The main advantages of both methods are that the exact amount of resin required may be applied and, since all the solution is used, there are no problems relating to the recovery of resin solutions.

Experimental Procedure and Results

Pretreatment with Ethanolic Potassium Hydroxide

The procedure adopted for pretreating the wool with alcoholic alkali was as follows: The alcoholic alkali solution was prepared by adding the required quantity of approximately 50% aqueous potassium hydroxide to absolute ethanol, stirring well, and then adding sufficient water to bring the water content of the solution to 2%. With pilot-scale work, denatured absolute alcohol was used. The wool was steeped in this solution at 20°C for the required time. The liquor/wool ratio varied from 10:1 to 50:1 (v/w) depending on the concentration of the alkali. The wool was then removed from the solution, centrifuged, and immersed in aqueous 2*N* hydrochloric acid for about 10 min. to neutralize the alkali. (Dilute aqueous or alcoholic sulfuric acid can also be used.) It was then removed from the acid solution, neutralized with sodium bicarbonate solution, rinsed several times with water, and allowed to condition at 65% R.H. and 70°F. The time of pretreatment was taken from when the wool was immersed in the alkali solution until it was immersed in the acid. The fabric was then treated with the required amount of resin dissolved in 75% (v/v) ethanol (liquor/wool ratio, 2:1) by pressing, as described above.

TABLE I. AREA SHRINKAGE OF FABRIC PRETREATED WITH 0.075% KOH (W/V) IN 98% ETHANOL FOR 15 MIN., NEUTRALIZED, RINSED, CONDITIONED, AND TREATED WITH RESIN IN 75% ETHANOL (V/V)

Pretreatment	Area shrinkage (%) for: 0% Resin*	2% Resin	4% Resin
0.075% KOH at 25°C	45	31	5
0.075% KOH at 50°C	45	5	0
0.075% KOH at 75°C	45	1	0
Ethanol-extracted	38	9	1
No pretreatment	37	32	14

* % Resin is based on the weight of conditioned wool throughout.

The effect of varying the concentration of the resin solution for different alcoholic alkali pretreatments is shown in Tables I, II, and III.

When hot ethanol extraction was used as a pretreatment, approximately 3% resin was usually required to obtain zero shrinkage [1]. Taking this as a standard, it may be seen from Tables II and III that both 0.1% alcoholic potassium hydroxide for 30 min. and 1.0% potassium hydroxide for 2.5 min. are effective pretreatments.

However, it may also be noticed from Tables I–III that with somewhat longer treatments with alcoholic alkali, less resin is required to give adequate shrinkproofing.

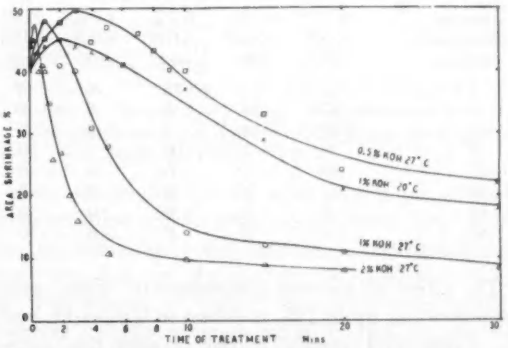

FIG. 1. *Effect of ethanolic KOH pretreatment on the felting shrinkage of wool fabric.*

TABLE II. AREA SHRINKAGE OF FABRIC PRETREATED WITH 0.1% KOH IN 98% ETHANOL AT 20°C, NEUTRALIZED, RINSED, CONDITIONED, AND TREATED WITH RESIN IN 75% ETHANOL

Time of pretreatment (min.)	Area shrinkage (%) for: 0% Resin	1% Resin	2% Resin	3% Resin
0	39	35	29	19
2.5	42	39	31	24
5	44	37	27	18
10	46	29	21	15
15	45	26	19	11
20	45	19	14	6
30	47	7	2	0
45	42	3	0	1
60	40	3	0	0

TABLE III. AREA SHRINKAGE OF FABRIC PRETREATED WITH 1.0% KOH IN 98% ETHANOL AT 20°C, NEUTRALIZED, RINSED, CONDITIONED, AND TREATED WITH RESIN IN 75% ETHANOL

Time of pretreatment (min.)	Area shrinkage (%) for: 0% Resin	1% Resin	2% Resin	3% Resin
0	40	37	30	21
2.5	45	16	3	0
5	42	8	1	1
10	37	4	2	0
15	29	1	0	0
20	21	0	1	0
30	18	0	0	0
45	11	0	0	0
60	12	1	0	0

TABLE IV. AREA SHRINKAGE OF FABRIC PRETREATED WITH KOH IN 98% ETHANOL AT 20°C, NEUTRALIZED, RINSED, CONDITIONED, AND TREATED WITH 1% RESIN IN 75% ETHANOL

Time of pretreatment (min.)	Area shrinkage (%) for: 0.1% KOH soln.	0.2% KOH soln.	0.5% KOH soln.	1.0% KOH soln.	2.0% KOH soln.
2.5	39	32	25	16	0
5	37	28	6	8	0
10	29	10	1	4	0
15	26	7	0	1	0
20	19	5	0	0	0
30	7	4	0	0	0
45	3	0	0	0	0
60	3	4	0	0	0

The effect of varying pretreatments, using resin concentrations up to 1%, is shown in Tables IV and V. From these results, it may be seen that satisfactory reduction in felting shrinkage can be achieved using very small quantities of resin.

TABLE IIa. AREA SHRINKAGE OF FABRIC PRETREATED WITH 0.1% KOH IN 98% ETHANOL, THEN IMMEDIATELY TREATED WITH RESIN IN ABSOLUTE ETHANOL

Time of pretreatment (min.)	Area shrinkage (%) for: 0% Resin	1% Resin	2% Resin	3% Resin
2.5	41	34	30	28
5	43	20	6	5
10	42	16	6	3
15	38	6	0	0
20	34	5	0	0
30	30	2	0	1
45	36	0	0	0
60	32	1	0	0

TABLE IIIa. AREA SHRINKAGE OF FABRIC PRETREATED WITH 1.0% KOH IN 98% ETHANOL, THEN IMMEDIATELY TREATED WITH RESIN IN ABSOLUTE ETHANOL

Time of pretreatment (min.)	Area shrinkage (%) for: 0% Resin	1% Resin	2% Resin	3% Resin
2.5	25	4	0	0
5	8	0	0	0
10	7	0	0	0
15	4	0	0	0
20	4	0	0	0
30	5	0	0	0
45	8	0	0	0
60	10	0	0	0

TABLE IVa. AREA SHRINKAGE OF FABRIC PRETREATED WITH KOH IN 98% ETHANOL AT 20°C, THEN IMMEDIATELY TREATED WITH 1% RESIN IN ABSOLUTE ETHANOL

Time of pretreatment (min.)	Area shrinkage (%) for: 0.1% KOH soln.	0.2% KOH soln.	0.5% KOH soln.	1.0% KOH soln.	2.0% KOH soln.
2.5	34	17	16	4	0
5	20	5	2	0	0
10	16	3	1	0	0
15	6	0	0	0	0
20	5	1	1	0	0
30	2	0	1	0	0
45	0	0	0	0	0
60	1	0	0	0	0

The effect on the felting shrinkage of wool of varying pretreatments with alcoholic alkali alone is shown in Figure 1.

Pretreatment without Neutralizing

It would be preferable if the aqueous neutralization step could be omitted; since both the pretreatment and the resin treatment use alcoholic solutions,

TABLE V. AREA SHRINKAGE OF FABRIC PRETREATED WITH KOH IN 98% ETHANOL AT 20°C, NEUTRALIZED, RINSED, CONDITIONED, AND TREATED WITH RESIN IN 75% ETHANOL

Pretreatment		Area shrinkage (%) for:			
KOH (%)	Time (min.)	0% Resin	0.25% Resin	0.5% Resin	1.0% Resin
0.5	20	43	6	1	0
1.0	10	29	2	2	0
2.0	5	40	2	0	0
3.0	3	30	3	0	0
5.0	1	44	4	2	2

TABLE Va. AREA SHRINKAGE OF FABRIC PRETREATED WITH KOH IN 98% ETHANOL AT 20°C, THEN IMMEDIATELY TREATED WITH RESIN IN ABSOLUTE ETHANOL

Pretreatment		Area shrinkage (%) for:			
KOH (%)	Time (min.)	0% Resin	0.25% Resin	0.5% Resin	1.0% Resin
0.5	20	12	5	0	0
1.0	10	15	5	0	0
2.0	5	25	3	0	0
3.0	3	26	3	0	0
5.0	1	29	4	0	0

it seemed that this might be feasible. Therefore, after removing the wool from the alcoholic alkali solution and centrifuging, the resin was applied by immediately pressing the wool into the resin solution, as described above. The alcohol was evaporated, and the resin was hydrolyzed and the alkali neutralized by steeping the fabric in 2*N* hydrochloric acid for ¾ hr. in the usual way. Results obtained by this method of treatment are given in Tables IIa–Va, which correspond with Tables II–V, respectively.

In this procedure, absolute alcohol was used as a solvent for the resin, although as much as 5% water could be present in the resin solution without the wool suffering any damage. The time of pretreatment was taken from when the wool was immersed in the alcoholic alkali solution until it was pressed into the resin solution. The times given in Tables IIa–Va are not strictly comparable with those in Tables II–V because after the wool was centrifuged, approximately 8 min. elapsed while the resin was applied and the wool dried before the wool was immersed in the 2*N* hydrochloric acid.

Combined Treatment with Alcoholic Alkali and Resin

Since both alkali and resin are soluble in alcohol, it is feasible to assume that the wool could be treated by immersion in an alcoholic solution containing both the alkali and the resin. This can be done using conditions similar to those of Tables IIa–Va. The amount of resin in the solution was adjusted so that after centrifuging or mangling, the required quantity was left on the wool. Examples of this method have been published elsewhere [3].

However, this method suffers from the disadvantages of the steeping and mangling technique outlined above, and therefore the pressing technique was applied to the combined treatment. The procedure was to dissolve the resin in absolute ethanol, cool, and then add the required amount of 50% aqueous potassium hydroxide solution. The liquor/wool ratio was 2:1, and the quantity of KOH was based on the weight of wool. The wool was quickly pressed into the solution at 20°C, left for the required time, and then dried for 5 min. with a current of cool air and hydrolyzed as above.

TABLE VI. AREA SHRINKAGE OF FABRIC TREATED BY PRESSING IN A COMBINED RESIN-KOH SOLUTION IN 98% ETHANOL AT 20°C FOR 30 MIN.

	Area shrinkage (%) for:			
KOH* (%)	0% Resin	1% Resin	2% Resin	3% Resin
0.1	44	39	33	35
0.25	42	18	7	6
0.5	36	5	1	0
0.75	37	4	1	0
1.0	34	4	3	0
1.5	36	8	0	0
2.0	34	12	3	0
3.0	37	11	2	0

* % KOH for combined treatments is based on the weight of wool. The liquor/wool ratio was 2:1.

TABLE VII. AREA SHRINKAGE OF FABRIC TREATED BY PRESSING IN A COMBINED RESIN-KOH SOLUTION* IN 98% ETHANOL AT 20°C

Pressing time (min.)	Area shrinkage (%) for:			
	0% Resin	1% Resin	2% Resin	3% Resin
2.5	44	31	18	11
5	38	23	8	2
10	34	16	1	0
15	31	4	0	0
20	31	4	1	0
30	42	3	0	1
45	44	9	1	1
60	41	7	2	1

* The concentration of KOH was 0.75% (on the weight of wool). The liquor/wool ratio was 2:1.

TABLE VIII. AREA SHRINKAGE OF FABRIC TREATED BY PRESSING IN A COMBINED RESIN-KOH SOLUTION* IN 98% ETHANOL AT 20°C

KOH† (%)	Area shrinkage (%) for pressing times of: 2.5 min.	5 min.	10 min.	20 min.	30 min.	60 min.	120 min.
0.1	38	39	36	38	39	39	37
0.25	41	35	28	26	18	14	21
0.5	35	29	19	6	5	10	20
0.75	31	23	16	4	4	7	17
1.0	24	12	6	7	4	20	36
1.5	12	3	1	9	8	19	37
2.0	4	2	5	6	12	17	37
3.0	0	2	3	10	11	25	44

* The concentration of resin was 1%.
† % KOH is based on the weight of wool. The liquor/wool ratio was 2:1.

This process was found to be quite effective, and has been used successfully on both the pilot and industrial scale. A disadvantage with bulk treatment results from the rapid absorption of alkali by the wool, so that during pressing much of the alkali is absorbed from the solution as it diffuses up through the material. Therefore, unless the goods are pressed into the solution extremely rapidly, those on top of the load tend to be undertreated.

Tables VI–VIII show the effect of varying the concentrations of resin and KOH, and the pressing time.

Discussion

The above results show that the felting of wool may be eliminated by treatment with extremely low concentrations of alkoxymethyl polyamide resins if either the wool is first treated with alcoholic potash solutions, with or without subsequent neutralization, or the alkali is incorporated in the alcoholic resin solution. Using the pretreatment method, better results are obtained if the wool is not neutralized after the alkali treatment, probably because the alkali continues to react with the wool during drying until the alkali is converted to carbonate.

As little as 1% resin on the wool is sufficient to prevent felting shrinkage when a suitable pretreatment is used, while a combined treatment requires about 2% resin to eliminate felting unless a relatively high concentration of alkali is used for a very short time. These resin concentrations are considerably lower than that required to eliminate the felting of alcohol-extracted fabric (approximately 3%). It should be noted that these alkali treatments do not by themselves appreciably affect the felting shrinkage of the wool, indicating that the alkali treatment is a more effective pretreatment than alcohol-extraction. It has been shown previously [2] that both fiber-cleansing and fiber-surface modification can be effective pretreatments for resin deposition because both tend to improve resin-fiber adhesion. It appears from the above results that fiber-surface modification has a greater effect than fiber-cleansing. Although both may occur with the pretreatment method, only fiber-surface modification is operative in the combined treatment using the pressing technique, since all the liquor is allowed to dry onto the wool. It has been shown that alcoholic alkali causes pitting of the fiber surface [6], and it is thought that the increased resin-fiber adhesion produced by this surface roughening enables smaller amounts of resin to be effective in preventing felting.

Tables II and III and Figure 1 show that the felting shrinkage first increases with increasing time of alkali treatment, and then decreases. This behavior does not appear to have been reported elsewhere for alcoholic alkali treatment, but it has been observed with the action of hydrogen peroxide solutions on wool [2].

Inspection of the data for 1% resin in Table VI shows that the shrinkage reaches a minimum value when 0.75%–1.0% potassium hydroxide is used. This effect, which is not evident when greater amounts of resin are used, was first thought to be due to greater quantities of KOH acting as a contaminant and interfering with the resin deposition. However, the data in Table VII for 1% resin show that the effect is governed by time, shrinkage tending to increase with time of pressing beyond about 30 min. Consequently, it cannot be due to interference with deposition by excessive amounts of KOH, which would not be time-dependent. This is also illustrated by the results in Table VIII, which again show increases in shrinkage with extended times of pressing. Thus, for a given concentration of KOH, there is an optimum pressing time. The experiments reported in Table IX were undertaken to find a possible explanation for the above effect. Comparison of treatments 1 and 4 shows that this effect is not due to gelling of the resin during treatment or to reaction of the KOH with the resin. By comparing treatments 5 and 6 with 1, it may be seen that rinsing with alcohol or neutralizing and rinsing before applying the resin renders the treatment effective. Therefore, it is considered that the increase

TABLE IX. EFFECT OF VARIATIONS IN TREATMENT WITH 3% KOH* BY THE COMBINED METHOD ON THE FELTING SHRINKAGE OF FABRIC

Treatment	Area shrinkage (%)
1. Press with 3% KOH-1% resin for 60 min. at 20°C, air-dry, etc. (see text)	28
2. As for 1, but resin omitted	42
3. As for 1, but press for only 2.5 min.	0
4. Press with 3% KOH for 60 min. at 20°C, add 1% resin just before drying	22
5. As for 4, but rinse with alcohol before adding resin	1
6. As for 4, but neutralize, rinse, and condition before adding resin	0
7. As for 6, but air-dry before neutralizing	14
8. No pretreatment; 1% resin	38
9. Untreated control	40

* % KOH is based on the weight of wool. The liquor/wool ratio was 2:1.

in shrinkage with increasing time of pressing is due to interference with resin deposition by decomposition products of the wool produced by excessive alkali treatment. Treatment 7 indicates that, if the wool is dried before neutralizing, some of the decomposition products are rendered insoluble and so remain to interfere with the deposition of the resin. In the two-bath treatment, overtreatment with KOH is not shown by the reduced effectiveness of the resin deposit, because any decomposition products are dissolved in the KOH solution and/or removed by centrifuging before the resin treatment. Therefore, in this case, excessive pretreatment with KOH merely results in effective shrinkproofing being obtained with reduced amounts of resin, as the KOH itself contributes towards reducing the shrinkage. Since the effectiveness of the pretreatment is enhanced by not neutralizing before application of the resin, it is apparent that there is little or no accumulation of decomposition products on the wool. This indicates that damage, if any, during drying has been slight.

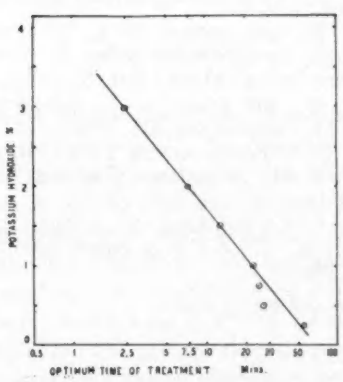

FIG. 2. *Optimum times of treatment by the combined method to prevent felting shrinkage of wool fabric. % KOH is based on the weight of wool; liquor/wool ratio, 2:1.*

It has been shown that shrinkproofing with alcoholic alkali does not have a deleterious effect on the strength of the wool [5]. Therefore, even when there have been sufficient decomposition products formed to interfere with the deposition of the resin, it is likely that the wool has suffered only negligible damage, since the times of pretreatment are considerably less than those recommended for shrinkproofing with alcoholic alkali [4].

The data of Table VIII were used to determine, for different alkali concentrations in the combined treatment, the times of pressing which result in the resin attaining its maximum effect. For each concentration of KOH, the area shrinkage was plotted against time of pressing, and the minimum of each curve was obtained. These minima are taken to represent the optimal times of treatment. When the logarithms of these times were plotted against concentrations of KOH (Figure 2), a straight line was obtained which could be used as a rough guide for pressing times for any concentrations of KOH. Assuming the alkali concentration remains constant (this will not hold when using extremely low concentrations in conjunction with low liquor/wool ratios, owing to absorption of alkali by the wool) and that the area shrinkage of the resin-treated fabric is proportional to the extent of reaction between the alkali and the wool, such an exponential relation between time and concentration would be expected. If we define an optimum pretreatment as one which results in little or no reduction in felting *per se* but enables the resin to attain its maximum effect, it is obvious that the point of optimum pretreatment occurs where the shrinkage-time curve (Figure 1), after having passed the maximum, crosses the line representing 40% area shrinkage. For example, for 1% KOH at 20°C, this point occurs at a treatment time of about 7 min. (Figure 1). It may be seen in Figure 2 that this time corresponds with a similar concentration of KOH, bearing in mind that the concentration of KOH is based on the weight of wool and the liquor/wool ratio is 2:1, so that 1%

KOH solution is equivalent to 2% KOH in Figure 2. Therefore, it appears likely that for a given temperature the conditions of alkali treatment apply equally well to both pretreatment and combined methods. It is probable that for temperatures other than 20°C the optimum time for both methods may be obtained from curves similar to those of Figure 1.

It may be noticed in Table VIII that, as the concentration of KOH decreases, the minimum value for shrinkage increases, indicating that a pretreatment with a high concentration of KOH for a short time is preferable to one with a low concentration for a long time. With the former, the action of the KOH would tend to be confined to the surface of the wool, which is one of the requisites of a pretreatment. When low concentrations of KOH are used for longer periods, then by the time the surface is suitably modified, sufficient decomposition products have been formed to interfere with the deposition of the resin. Alcoholic alkali has been used to pretreat wool prior to the application of melamine- and urea-formaldehyde resins to prevent felting shrinkage [7]. The reason why Pfeffer and Kitaj had to use high concentrations of KOH (7.5% for 5 min. or 4% for 10 min.) was probably because they used absolute alcohol as a solvent. The presence of a small amount of water in the alcoholic alkali solution enables much lower concentrations of alkali to be used [4].

The amount of resin required to give shrinkproofing also depends on the wool and the type of fabric used. For example, in pilot-scale work on half-hose using the pretreatment conditions in Tables V and Va, 1% resin was required to give zero shrinkage, whereas the fabric used in the work reported here required only 0.5% resin.

Conclusions

(*1*) Alcoholic potassium hydroxide is an effective pretreatment in the application of alkoxymethyl polyamide resins to prevent the felting shrinkage of wool.

(*2*) After pretreatment, the wool may be neutralized, rinsed, and conditioned, or the resin treatment may directly follow the pretreatment without neutralizing the wool. The alkali can also be incorporated in the resin solution, so that pretreatment and resin treatment are combined.

(*3*) It is better to use a relatively high concentration of KOH for a short time rather than a low concentration for a long time because in the former case, the action of the KOH will tend to be confined to the surface of the wool and thus give a more efficient pretreatment.

(*4*) If the time of pretreatment is extended in order to reduce the amount of resin required, decomposition products of the wool will interfere with the deposition of the resin unless they are removed before the resin is applied. If this is done, as little as 0.5% resin will eliminate felting.

(*5*) A pretreatment which does not in itself reduce the felting shrinkage requires about 1% resin to confer unshrinkability on the wool. With a combined treatment, about 2% resin is required to give zero shrinkage unless relatively high concentrations of KOH are used for very short times.

Acknowledgment

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The Action on Wool Fibers of Strong Solutions of Urea Containing Reducing Agents

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Contribution of Textile Research Institute, Princeton, N. J., and Textile Department, University of Leeds, England

Introduction

A number of soluble high-molecular-weight derivatives of keratins have been prepared with the object of elucidating further the structure of the original insoluble substance. The results of these studies have been reviewed by Ward [21], and, to judge from his data, it is clear that a considerable variety of derivatives is possible. These products differ in molecular weight and shape and seem to owe their origin to the fact, demonstrated in other ways, that the cystine cross-linkages differ in their susceptibility to reduction [18]. Probably also some peptide bonds may be particularly liable to hydrolysis. The present article concerns the properties of the protein extracted from wool fiber by means of strong solutions of urea containing reducing agents. The molecular characteristics of this material have been discussed elsewhere [14, 17, 21, 23]. Here attention will be directed toward the fraction of the wool which is dissolved, the nature of the undissolved residue, and the fiber-forming properties of the regenerated keratin derivatives.

Experimental

Materials

Lincoln or Merino wool, solvent extracted, was used in all experiments. The chemical reagents were of a "chemically pure" grade. A solution saturated with respect to urea was prepared by adding solid urea in excess to water at 22°C. To 100 ml. of the saturated solution of urea was added either 5 g. of solid sodium metabisulfite or 2 g. of thioglycolic acid (in the form of a 90% solution of the acid in water). The pH was then adjusted to 8 by the addition of solid sodium bicarbonate or carbonate as required. Solid urea was added to the final solution to maintain saturation during storage at the room temperature of 22°C.

X-Ray Patterns

Patterns were made using filtered Cu Kα-rays, and the distance from film to specimen was 4.0 cm. The characteristic patterns, which will be referred to in the text, have frequently been described and reproduced by Astbury and his collaborators. These patterns are: (*a*) the α pattern, and (*b*) the parallel β pattern [3]; (*c*) the disoriented α pattern, (*d*) the disoriented β pattern, and (*e*) the cross β pattern [4, 19]. A further vague pattern consisting of two halos centered about 10 Å. and 4.5 Å. but distinct from (*c*) and (*d*) will be referred to as the "diffuse halo pattern."

Optical Properties

Birefringence of fibers was measured using a Sénarmont compensator [9] mounted on an ordinary microscope. Unless otherwise stated, the materials were usually dehydrated in a succession of aqueous solutions of increasing concentration of ethyl alcohol and mounted in *o*-dichlorobenzene for the actual measurement.

Preparation of Soluble Derivatives

As will be discussed later, the properties of the extracted protein depend upon the conditions of extraction, which seem to determine the degree to which the protein first removed from the fiber is converted into a further derivative of different character. The two methods of preparation, which are described below, have been found to give predominantly one type of extracted protein or the other; but in most cases some mixture of the two results, and the first extract readily changes into the second.

Primary unorientable extract.—Ten grams of wool was added to 100 ml. of urea-reducer solution, and the whole was maintained at 40°C for 24 hrs. Usu-

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ally about 20%–25% of the wool dissolved, giving an extract approximately 2% in protein. The dissolved protein could be reprecipitated as a white, poorly cohering precipitate by the addition of sufficient acetic acid to bring the pH into the range 4–5. When approximately one part of saturated ammonium sulfate was added to four parts of the urea extract, the protein was precipitated as a grey, tacky curd resembling chewing gum. There was a marked resemblance to regenerated feather keratin [13] and to epidermin (see preparation described below). The gumlike curd readily cohered into a single lump and could be drawn into tapering threads. These threads showed no fibrous aspects, were not birefringent, and gave an unoriented diffuse halo-type x-ray pattern. For this reason the extract will be referred to as the "unorientable extract." No free thiol groups were detected in the regenerated solid using nitroprusside, but these appeared after treatment with potassium cyanide.

Orientable extracts.—When solutions of the above preparation were allowed to stand for 2 weeks at room temperature, the pH of the solution increased to between 9 and 10, and the solution acquired a strongly ammoniacal odor. The character of the protein, precipitated from the solution by the addition of ammonium sulfate to aliquots, changed progressively. The change appeared complete in about 2 weeks. The precipitated protein formed a white, gelatinous, coherent curd with fibrous characteristics. After pressing out excess solvent, the precipitate could readily be drawn into strong threads. When washed and dried, these formed clear, pliable, birefringent filaments ($n_2 - n_1 = 0.006$-0.007; original wool, 0.01) with a marked mechanical anisotropy. After storing for some weeks, these filaments darkened and became brittle.

X-ray patterns of such filaments usually showed good orientation of the strong 10 Å. equatorial spots, with poorly developed axial arcs at 5.1 Å (α-type patterns). Commonly, traces of the 4.5 Å. β-type reflection were found both on the equator (parallel β) and on the meridian (cross β). Stretching the filaments in water did not improve the orientation nor effect a conversion into a fiber yielding a parallel β-type pattern. Swelling in water was marked, and the internal coherency of the swollen fiber seemed poor, which may account for the inability to effect the transformation.

The same kind of extract was obtained in one step by maintaining the bath at 65°C during extraction. Ammonia was evolved for some 48 hrs., after which the extraction was terminated. The protein extracted under these conditions amounted to between 40% and 45% of the wool. In fibrous form the orientable derivative showed a strong affinity for basic dyes.

Paper chromatograms of the two types of derived protein appeared identical and were very similar to those of the original wool.

Preparations of the prekeratin from skin—epidermin [19]—and of oxidized keratin [1] were made for purposes of comparison with the reduced keratins.

Epidermin [19].—Pieces of the thick skin cut from a cow's nose were covered with saturated urea and allowed to stand for 24 hrs. at room temperature. The undissolved material was then centrifuged off, leaving an extract of the prekeratinous protein of the germinal layers. The protein was precipitated by the addition of ammonium sulfate to one-quarter saturation. The properties of the material were remarkably similar to those of the orientable keratin derivatives.

Oxidized keratin (*keratose* [2]).—Five grams of chopped wool was added to 100 ml. of 1% peracetic acid in water and allowed to stand for 24 hrs. at room temperature. The oxidized wool was then washed and extracted with 1% ammonia for 8 hrs., after which time the undissolved residue was centrifuged off.

When precipitated from solution with ammonium sulfate, a tacky, grey, fibrous curd strongly resembling the orientable type of extract described above was obtained. Drawn filaments were birefringent and yielded a good, well-oriented α-type x-ray pattern.

Observation of Fibers During Extraction

When placed in the urea-reducer solution, wool fibers undergo a series of changes in over-all shape which accompany the process of extraction. It was found best to use short lengths of fiber (0.1–0.2 mm.) when observing the phenomenon. At approximately 40°C short lengths curled into arcs in a few minutes due to a contraction (supercontraction [22]) of one side of each filament. During this change the birefringence of the contracting side fell to a low value ($\simeq 0.001$ in *o*-dichlorobenzene); that of the other side remained unchanged (see Figure 1). Longer lengths of fiber curled into coils. Over the next few hours, particularly when the tem-

perature was raised to 65°C, the other side of most fibers also contracted, with a fall in birefringence, and the fiber straightened, assuming an over-all shorter length. The contraction measured on lengths of fiber about 5 cm. long varied between 20% and 30%, which is similar to the order of supercontraction noted by others [20, 22]. Subsequent to these changes the whole fiber swelled slowly, and during this stage the greater part of the extraction of protein seemed to occur.

When short lengths of curled fibers were removed from the urea solution, washed, and mounted in water, they curled in the opposite direction owing to the greater swelling of the altered half of the fiber. The other half (now inside the arc) remained birefringent and apparently unaltered. Within the swollen, isotropic portion of the cortex could be seen the striated outlines of the cortical cell membranes [15]. On digesting such material in trypsin (commercial, buffered pH 8.6 at 40°C), the isotropic swollen half was removed, leaving a resistant cuticular sheath and the unaltered birefringent strand. These observations may be compared with those described by the author in the case of other methods of supercontraction of wool which have led to a distinction between the more easily supercontracted half of the fiber, called the *orthocortex*, and the more stable portion, the *paracortex* [15] (see also [11]).

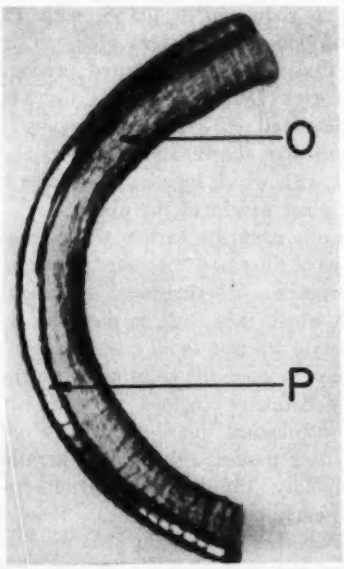

FIG. 1. *Photomicrograph of a short length of wool fiber during treatment in saturated urea containing a reducing agent. The orthocortex,* O, *has been disoriented and has supercontracted; the resistant paracortex,* P, *remains unaffected. The fiber has curled into an arc owing to the unilateral contraction (partly polarized light).*

These experiments revealed a considerable difference in behavior between individual fibers derived from the same staple. The time of curling, amount of curling, and the time for uniform contraction varied from fiber to fiber.

X-Ray Diffraction Patterns from the Insoluble Residue

(*a*) The insoluble residue of uncontracted paracortex (plus cuticular sheath), obtained by enzymatic digestion of "half" contracted fibers, gave a poorly oriented α pattern. The poor orientation seemed due to mechanical factors, the tendered fibers being difficult to parallelize.

(*b*) The insoluble, contracted fibers after extraction by the urea solution and after washing and drying gave a diffuse disoriented pattern in which halos corresponding to 10 Å. and 4.5 Å. were measurable. On stretching to 1.5 and 1.7 times the original length of the fibers, a poorly oriented cross β pattern developed. Stretching effected little improved orientation. Frequently mixed cross and parallel β patterns were noted.

(*c*) After extraction of oxidized wool by means of ammonia, the residue, consisting of the resistant cuticular sheath and the membranes of the cortical cells, gave an unoriented β pattern, confirming Happey's observation [1, 7]. This material may be responsible for certain of the β-type reflections in the residue after urea-extraction.

Further X-Ray Observations on Regenerated Keratin Derivatives

(*a*) *Various unoriented precipitates.*—The protein at first extracted from wool by urea, however regenerated (by weak acids, alcohol (50%), or ammonium sulfate), when washed and pressed yielded the "diffuse halo pattern."

(*b*) *Stability of the unorientable extracts.*—Boiling these precipitates in water for 20 min. did not lead to a different pattern. In particular, no β spacings developed.

(*c*) *Effect of blocking SH groups.*—Thiol groups of the unorientable extract were blocked by adding

to the solution in urea before precipitation ethyl bromide in excess of that required to saturate the solution, or, alternatively, 1 g. of iodoacetic acid to each 100 ml. of extract. On addition of ammonium sulfate, white, poorly coherent precipitates lacking fibrous properties were formed. When washed, pressed, and boiled with water for 20 min., these precipitates yielded very sharp, unoriented β patterns.

Swelling of Regenerated Keratin Derivatives

The swelling of pieces of drawn filaments of unorientable protein, orientable protein, and epidermin was compared by placing them in flat dishes containing a succession of buffers of differing pH values and making measurements on enlarged images. The swelling of the orientable extract and the epidermin was anisotropic; that of the unorientable protein was isotropic. In the pH range 5–8 the orientable extract exhibited a remarkable sensitivity to pH (see Figure 2). At pH 5 it formed a strong, white, condensed, elastic thread; at pH 8 it swelled remarkably to a glassy, brittle, gelatinous cylinder. Threads (1 mm. in diameter) exhibiting this large, anisotropic, reversible swelling were able to raise and lower weights of 5 g. when the pH was cycled between 5 and 8. Similar experiments have been described using threads of polyacids, and such preparations have been proposed as models of muscle.

Discussion

Fraction of Wool Dissolved by Urea-Reducer Solutions

Jones and Mecham [12] found that urea solutions containing reducing agents were able to dissolve only part of various keratinized tissues at moderate pH values. The observations described above show

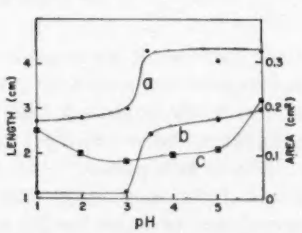

FIG. 2. *The relations between swelling and pH of the regenerated keratin derivatives.* a—*Length of fiber (cm.) of the "orientable derivative."* b—*Area of the same fiber (cm.²).* c—*Length of fiber of the "unorientable derivative."*

that the fraction extracted from wool fiber has a definite histological location. It is removed from that part of the cortex of the fiber which has been shown by other experiments to be less stabilized and more reactive, and has been named the *orthocortex* [15]; the insoluble residue consists of (*a*) part of the cortex named the *paracortex*, (*b*) the cortical cell membranes of the orthocortex, and (*c*) the resistant cuticular sheath. The behavior of fibers in urea-reducer solutions is similar to their behavior in other supercontracting liquids—*i.e.*, the orthocortex contracts first and bends the fiber into arcs or spirals (according to the length of the filament), with a loss of birefringence in the orthocortex, which indicates a disorientation of the fibrous structure, as shown in Figure 1. At this stage of the reaction, the contracted orthocortex may be removed by enzymatic digestion, leaving the resistant paracortex and the cuticle.

Longer treatment or treatment at higher temperature causes contraction of the paracortex also, but this fraction still resists solution, suggesting that there are persistent cross-linkages in this region. It seems possible to identify these cross-linkages, resistant to reduction at pH 8, with Phillips' $(C + D)$ disulfide cross-linkages [18]. The $(C + D)$ linkages thus seem to be located predominantly in the paracortex [16]. At pH 11 the whole cortex can be dissolved [6], leaving a residue of the resistant cuticular sheath and the cortical cell membranes [1, 15], which together form about 7%–10% of the original weight of the fiber.

This work confirms earlier work which showed that the wool fiber and the other keratinized tissues contain fractions differing very considerably in the ease with which they may be dissolved [15]. The most resistant fraction in all cases consists of various membranes; in wool, the keratin itself forms two histologically definable regions differing in stability, but this histological distribution does not seem to occur in other tissues, although the keratin does exhibit solubility differences. Asymmetry appears limited to curly or crimped hairs. Reasons are advanced in another publication [16] to show that the differences in solubility of the keratin fractions correspond to degrees in keratinization—*i.e.*, to differences in degree of cystine cross-linking. One of the interesting conclusions to be drawn from the observation described above is that since there are considerable differences in the response of the individual fibers to urea-reducer solutions, these fibers differ in their

stability and therefore presumably in composition. This conclusion seems to be in harmony with those of Dry, Burley, and Speakman [5].

These findings have a bearing on the practical problem of solubilizing and regenerating keratins for commercial purposes. The yield of regenerated protein is not likely to exceed 90% due to the presence of the resistant membranes. In order to obtain a figure as high as this, it may be useful to effect solution in two steps of differing severity, possibly yielding fractions of different composition and molecular weight.

Molecular Configuration of the Resistant Fractions

When the orthocortex is removed by enzymatic digestion *before* the paracortex supercontracts, the x-ray pattern of the residue remains the α type. This demonstrates the stepwise nature of the reactions of the wool fiber and confirms the impressions gained from polarized microscopy. However, if the paracortex has supercontracted but not dissolved in the urea solution, the residue after washing and stretching may yield a cross β pattern. Thus the original α configuration has been lost during supercontraction and the loosened chains have been enabled to assume a β configuration. Cross β patterns have been obtained from other α proteins, such as myosin [4] and epidermin [19], but have not been obtained previously from wool keratin. The meaning of the pattern is obscure. Rudall [19] advanced certain suggestions which could explain the development of sets of planes of 4.5 Å. spacing in the appropriate direction, but the present work, apart from confirming the expectation that regenerated wool keratin is very similar to the prekeratin from the germinal layers, contributes little to the understanding of this problem. It may be significant that fibers yielding a cross β pattern could not be made to give a parallel β pattern by stretching.

The entire removal of keratin from the cortex leaves the resistant fraction of the cuticle and the cortical cell membranes, which give a disoriented β-type x-ray pattern. Happey [7] and Alexander and Earland [1] are of the opinion that this finding is to be accepted at its face value, and means that these membranes have a β structure in the intact fiber, and, further, that the insolubility is to be ascribed to this structure. The danger that the β structure is a secondary structure produced by the chemical treatment should be borne in mind, and the result needs to be confirmed by observations on membranes which have been obtained without chemical treatment.

Properties of the Extracted and Regenerated Keratin Derivatives

Particular interest attaches to the preparation of potentially fiber-forming derivatives and to the molecular configuration (α or β) of the regenerated fibers [8, 13]. A comparison of the properties of the two types of regenerated derivative prepared from the extraction of wool by urea solutions suggests the hypothesis that the protein, apparently removed from the orthocortex exclusively, is present at first in solution as randomly oriented chains (or more complex forms) with disulfide bridges largely reduced. When regenerated in this condition, the gumlike precipitate contains no detectable thiol groups and is insoluble in urea solutions unless reducers are present. The random configuration indicated by x-ray diffraction is stable in boiling water. On the other hand, when the free thiol groups are blocked in solution, the regenerated protein loses its sticky, coherent character and the β configuration can be produced by boiling the precipitated material with water. These facts imply that there is a re-formation of disulfide cross-linkages on precipitating the extracted protein, which stabilizes the random configuration and prevents the formation of well-organized crystallites. It seems reasonable to liken the randomly arranged cross-linked system of chains in such regenerated keratins to that prevailing in a phenoplast.

However, on allowing the solution to stand or on raising the temperature during extraction, a secondary reaction occurs which leads to the formation of a modified protein with contrasted physicochemical characteristics. This reaction is obscure, and no molecular weight or shape measurements are available relating to the change, but some suggestive findings are: (*a*) free ammonia forms slowly; (*b*) no new amino acid residues appear and, to the degree of approximation imposed by paper chromatography, the relative quantities of acids remain unchanged—in particular, little cysteic acid appears; (*c*) the derived protein possesses a pronounced acid character, shown by swelling and staining; and (*d*) oriented fibers are possible.

A suggestion which would relate these facts is that a progressive hydrolysis of the amide groups of the dissolved polypeptides to acid groups takes place. In 10^5 g. of wool there are 88 gram mol. of basic

residues, 50 gram mol. of acidic residues, and 100 gram mol. of acid amide residues [10]. The complete conversion of amide groups to acid would increase the acid/base ratio from 59/88 to 159/88, resulting in a polypeptide chain of predominantly acid character. At a pH between 8 and 9 these would be ionized, giving a chain richly studded with COO^- side-groups, which should be well extended in solution because of the electrostatic repulsion of these charges. The formation of orientable precipitates from such a material may be a consequence of the existence of extended chains before precipitation because there is a good possibility of these cohering laterally in relatively well-oriented bundles further stabilized by cross-linking on precipitation. That the small-scale molecular configuration is of the α type may be a solvent effect. The configuration of synthetic polypeptides has been shown to be influenced by the solvent.

The oriented fibers with the pronounced acid character swell remarkably in alkaline media and would, for this reason alone, be of little value commercially unless the acid groups were "covered" or further cross-linkages were introduced. In this respect, the orientable regenerated keratin derivative differs from the prekeratin (epidermin) extracted from the germinal layers of the skin—which in other respects it strongly resembles—and also from the protein as first dissolved from wool. The predominantly acid character of the polypeptides of the native keratin is reduced by the amidation of two thirds of the acid groups. It is also possible that H-bonding between opposing amide groups contributes a further variety of cross-linking in the native fiber, and that the destruction of this further contributes to the remarkable difference between the orientable regenerated derivative and the original keratin.

Summary

Saturated aqueous solutions of urea containing reducing agents dissolve about 25% of wool fiber at pH 8. The extracted protein is removed from the less stabilized fraction of the cortex—the orthocortex—and the residue consists of the cuticular sheath, the cortical cell membranes of the orthocortex, and the resistant paracortex. The paracortex may supercontract, but does not dissolve at pH 8 and 65°C. When re-extended, such residues yield cross β-type x-ray patterns.

The protein first dissolved at room temperature when regenerated is a tacky, gumlike material devoid of fiber-forming properties. This protein in the urea solution at pH 8 is slowly converted into a derivative of very different properties. A similar preparation results when the original extraction is carried out at 65°C. This modified protein is strongly acid in character and may be formed into fibers yielding an α-type x-ray pattern. It is suggested that this change is due to the hydrolysis of the acid amide groups of the native keratin to free acidic side-chains.

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Measurement of Dielectric Constant and Dissipation Factor of Raw Cottons*

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Abstract

By use of a suitable capacitance bridge and special condenser, the dielectric constant and dissipation factor at a frequency of 200 kc./sec. were measured for several varieties of cotton and for several types of trash removed during processing. Measurements were made at 70°F and 45%, 55%, and 65% R.H. The results are in fair agreement with those obtained by other workers.

THIS RESEARCH was part of a project on the cleaning and opening of cotton by the use of static electricity. Its objective was to determine whether or not there are differences in dielectric constant and dissipation factor for cottons and trash which might be used in the development of improved cleaning equipment for the cotton industry. The method used to determine dielectric constant is a more or less general one of comparing the capacity of a condenser with different amounts of cotton or trash between the plates with the capacity when the plates are spaced the same distance apart in air. To obtain results at different moisture contents, the humidity of the laboratory was controlled at different levels.

* A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract is being supervised by the Southern Utilization Research Branch of the Agricultural Research Service.

Apparatus

The apparatus for the measurement of the dielectric constant and dissipation factor consisted of a type 716-C General Radio Co. capacitance bridge, a model 640 Jackson Electrical Co. signal generator, a type 710 General Radio Co. precision capacitor, a type BC-348 Signal Corps radio receiver, an R.C.A. Junior Voltohmyst vacuum tube voltmeter, a type BC-221 Signal Corps heterodyne frequency meter, and the test condenser.

The capacitance bridge used was a Schering-type bridge with a frequency range from 30 cycles/sec. to 300 kc./sec. The signal generator provided a radio-frequency source of approximately 100 mv. output at 200 kc./sec. The frequency was maintained constant by periodic checks with the BC-221 frequency meter, which had previously been calibrated against WWV. An extremely sensitive null-

point indicator was obtained by modifying a BC-348 radio receiver to permit the use of the Voltohmyst as a signal strength meter. The precision condenser served as a balancing capacitor with the bridge for measuring capacitance by the substitution method. All connections in the experimental setup were made with shielded coaxial cables using polyethylene insulation. A block diagram of the apparatus is shown in Figure 1.

The test condenser was constructed as shown in Figure 2. The aluminum plates were turned to a diameter of 8 in. from $\frac{1}{4}$-in. sheet aluminum faced down to $\frac{3}{16}$-in. thickness. The steel posts supporting the upper plate were machined to the same height ± 0.01 in. The polystyrene insulators were adjusted to the proper length by the use of metal and sheet mica shims. Washers used to adjust the spacing of the condenser plates were carefully selected washers accurate to within 0.0004 in. in thickness. The aluminum plates were reinforced with $\frac{3}{4}$-in. steel to prevent warping of the plates when cotton was placed in the condenser. A Lucite ring was formed around the plates to prevent cotton or trash from extending beyond the edges.

Procedure

Five irrigated and two rain-grown varieties of cotton were selected for the test. The irrigated varieties were Acala 4–42 (staple length 1.31 in.), Amsack (staple length 1.62 in.), "C" cotton from New Mexico (staple length 1.00 in.), Mesilla Valley (staple length 1.49 in.), and Pima (staple length 1.67 in.); the rain-grown varieties were Coker 100 (staple length 1.27 in.) and DPL 15 (staple length 1.29 in.). A mixture containing equal samples of the seven varieties of cotton was tested, and acetate rayon and DuPont nylon were also tested. The cottons, the acetate rayon, and the nylon were run through a Shirley Analyzer to remove any trash present and to fluff the fibers thoroughly.

Trash was selected from the following wastes obtained from Dan River Mills: waste of #2 cleaning section, opening room; cotton from the waste of #2 cleaning section, opening room; trash, with some cotton, from the waste of #2 cleaning section, opening room; trash, with no cotton, from the waste of #2 cleaning section, opening room; trash from mill-mix picker motes, beater #1; waste, mill-mix picker motes, beater #3; and waste, mill-mix, $\frac{3}{4}$ bale level, card motes.

The substitution method for the measurement of capacitance consisted of first adjusting the precision condenser so that the bridge balanced at some particular value with the test condenser empty. The Lucite ring is an integral part of the test condenser, and remained in place for all measurements. Experimental tests and calculations were made to determine the edge corrections for the various spacings of the test condenser. Cotton or trash was then added between the plates of the test condenser, and the readings of the internal standard condenser and the dissipation factor dials were noted. The dielectric constant and the dissipation factor of the air-cotton mixture were calculated.

Preliminary tests were made to determine reproducibility. The test condenser was filled with 6.7% cotton by volume for each test. Tests were made for all seven varieties of cotton at five different test condenser spacings, for seven different samples of Mesilla Valley cotton at the same condenser spacing, and for a sample of Pima cotton which was thoroughly refluffed and measured ten times. The dielectric constants of the air-cotton mixtures were

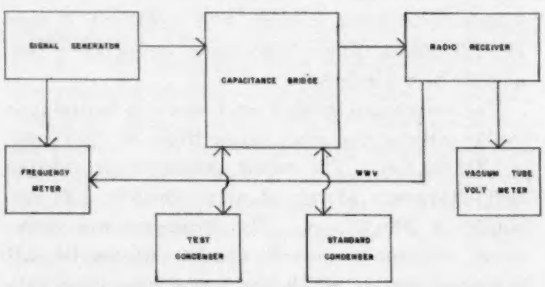

FIG. 1. *Block diagram of circuit.*

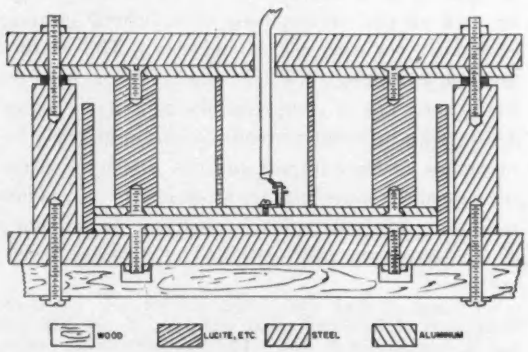

FIG. 2. *Test condenser.*

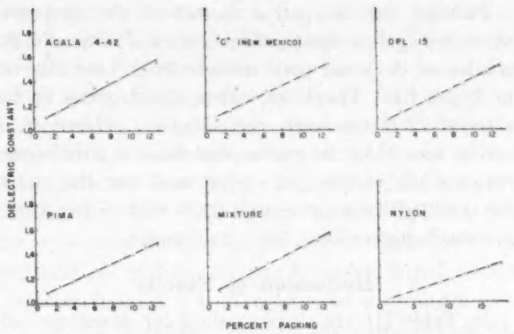

FIG. 3. *Plots showing the experimentally determined values of dielectric constant for four varieties of cotton, a mixture of all seven varieties of cotton, and nylon. (70°F, 55% R.H., 200 kc./sec.)*

calculated along with the standard deviations and standard errors. The results indicated that the variations were well within the experimental error of the bridge.

The tests on the several cottons and trash were conducted at 70°F and 55% R.H. They consisted of adding 5 g. at a time to the test condenser and reading the change in the capacitance and dissipation factor dials. It was possible to obtain up to 12.9% packing for cotton with a condenser spacing of 0.2913 in. The % packing refers to the % volume of the test condenser filled with cotton fiber, assuming a density of 1.55. The dielectric constant and the dissipation factor of the air-cotton mixtures were plotted against the % packing of cotton or trash in the test condenser with 0.2913 in. spacing. The dielectric constant of the various mixtures between 1.3% and 12.9% packing varied linearly with the weight of the cotton in the test condenser. The observations gave points which fell practically on a straight line (Figure 3). Under the assumption that this relation holds up to 100% packing, it would be possible to extrapolate values for the dielectric constant.

Straight lines were fitted to the experimental points by the method of least-squares, and the values of the dielectric constant for 100% packing were computed. An average extrapolated dielectric constant of 4.79 for the seven cottons (see Table I) was obtained, with a standard error of 0.15. This would indicate there was little, if any, difference between the cottons. A mixture of equal amounts of all seven cottons gave a dielectric constant of 4.89, which is very close to the mean of the individual values. The average dielectric constant for the various wastes was 6.55, with a standard error of 0.37.

With 6.7% packing at the five different spacings of the test condenser, the average dielectric constant for all tests was 1.270, with a standard error of .007. This gives further indication that there is practically no difference between the different varieties of cotton.

The plot of dielectric constant of trash against packing factor in the test condenser (Figure 4) was approximately linear when the cotton content was high. With no cotton present in the trash, the curve had an upward bend; it would be difficult to determine accurately by extrapolation a value for 100% packing. The approximate values listed were obtained by assuming that the trash had the same density as cotton, and by using only the last few points of the curves in the calculations. However, it can be seen that the dielectric constant for trash is much higher than that for cotton. Results for five types of trash are also shown in Table I.

To determine the effect of moisture content, the following varieties of cotton and types of trash were

TABLE I. EXTRAPOLATED VALUES FOR DIELECTRIC CONSTANT (70°F, 55% R.H., 200 KC./SEC.)

Acala 4–42	4.90	Acetate rayon	3.14
Amsack	4.25	DuPont nylon	2.79
"C" cotton from New Mexico	4.85	Trash (with some cotton) from waste of #2 cleaner section, opening room	6.61*
Coker 100	5.44		
DPL 15	4.64		
Mesilla Valley	5.02	Trash, mill-mix picker motes, beater #1	7.57
Pima	4.45		
		Trash from gyrator waste	6.09
Average	4.79	Waste, mill-mix picker motes, beater #3	7.12
Standard deviation	0.36		
Standard error	0.15	Waste, mill-mix, 3/4 bale level, card motes	5.45
Mixture of all 7 cottons	4.89		

* A straight line was assumed for all points above 30 g. in the condenser.

selected for the tests at 45%, 55%, and 65% R.H.: Acala 4–42 (medium staple length); "C" (short staple length); Pima (long staple length); trash (with some cotton) and trash (with no cotton) from the waste of #2 cleaner section, opening room; and mill-mix picker motes, beater #1. All these tests showed large increases in dielectric constant for higher relative humidity. The results at 55% R.H. disagree slightly with those in Table I since the tests were run at different times. Successive values at any one time give a smooth curve, but do vary somewhat when the test is repeated. See Table II and Figures 5 and 6.

Two runs through the Shirley Analyzer separated 33.6% cotton from the waste of #12 beater, opening room. A test of the original waste and the trash remaining after the cotton was removed indicated the dielectric constant of the trash to be higher than that of the waste, and the dielectric constant of the waste to be higher than that of the cotton. It might be possible to determine the amount of trash present by measurements of this type.

Plotting the dissipation factors of the air-cotton mixtures against the packing factors of cotton in the condenser does not give straight lines (see Figures 4, 5, and 6). Therefore, extrapolated values of the dissipation factor were not obtained. However, it can be seen from the curves that there is a difference between the varieties of cotton, and that the values for trash with no cotton and trash with picker motes are much higher than for cotton alone.

Discussion of Results

In Table III are shown values for dielectric constant obtained by other workers for cotton and some other fibers. It is seen that our extrapolated value of 4.79 for cotton at 55% R.H. (6.2% moisture) is lower than that obtained by Balls [1].

Balls' results were obtained by using a straight-line extrapolation with two points—the dielectric constant (unity) of the air condenser and the measured dielectric constant for 24% packing. This result can be obtained by using the formula $E_m - 1 = P(E - 1)$, where E_m is the dielectric constant of

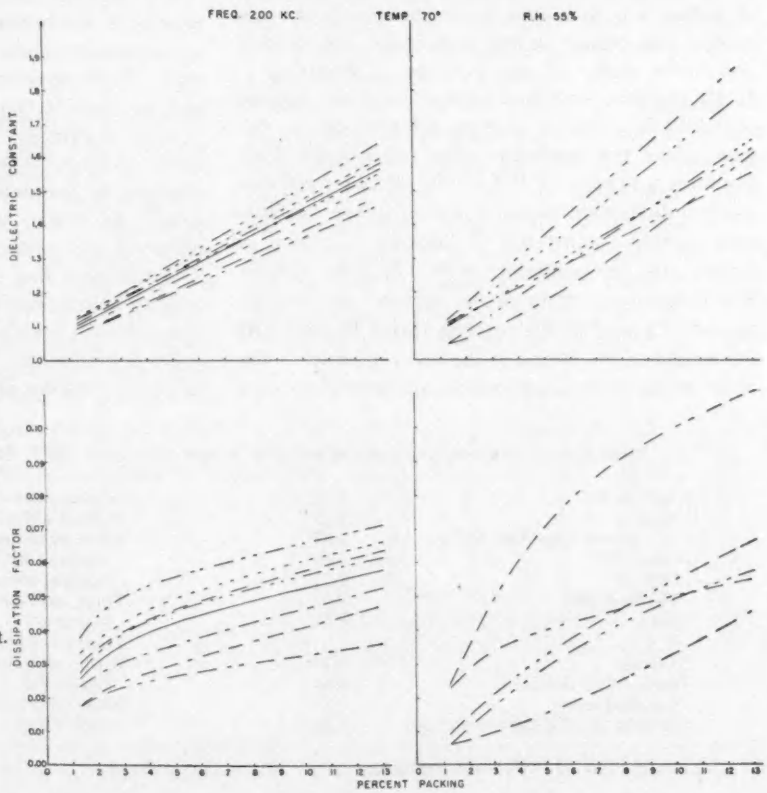

FIG. 4. *Dielectric constant and dissipation factor for several varieties of cotton and trash (70°F, 55% R.H., 200 kc./sec.): — - — - —, Coker 100; - - - - - -, Mesilla Valley; — — — — —, Acala 4–42; ————, mixture; — - — - — - —, "C" (New Mexico); — — — — —, DPL; — — — — — —, Pima; — — — — — — —, Amsack; — — — — —, trash with picker motes; — - — - —, waste with picker motes; — — — — — —, trash from gyrator waste;* — — — —, trash from waste (no cotton); — — — —, trash from waste (some cotton);* — - — - — -, waste from card notes; — — — — — —, cotton from waste.*

* Same line for dielectric constant.

the air-cotton mixture, E is the dielectric constant of cotton, and P is the packing factor. Balls also obtained data for transverse fibers using 41% packing which gave results somewhat lower than those for 24% packing. A dielectric constant of 4.2 was obtained with a moisture content of 5.4%, 4.4 with a moisture content of 6.2%, and 6.0 with a moisture content of 7.5%. The results seem to indicate that there is some bending of the curve of the dielectric constant *vs.* packing factor; however, based on the data we obtained it is thought to be very slight after 1% or 2% packing. Hence, our extrapolation for the dielectric constant is calculated on the basis of the ten values for dielectric constant obtained between 1.3% and 12.9% packing. Using the same method as Balls, with unity and the dielectric constant at 12.9% packing, would raise the average value of the dielectric constant from 4.79 to 5.12.

The dielectric constants for nylon and acetate rayon fibers were calculated by four different methods, using in each case the values for dielectric constant of the air-fiber mixture for ten different packing factors. These methods were: (*1*) straight-line extrapolation; (*2*) equation by Balls, $E_m - 1 = P(E - 1)$; (*3*) Lorentz' [7] equation for mixtures,

$$\frac{E_m - 1}{E_m + 2} = \frac{P(E - 1)}{E + 2};$$

and (*4*) Lichtenecker's [6] equation for mixtures, $\log E_m = P \log E$.

No consistent results for cotton fibers could be obtained by using either the Lorentz or Lichtenecker equations.

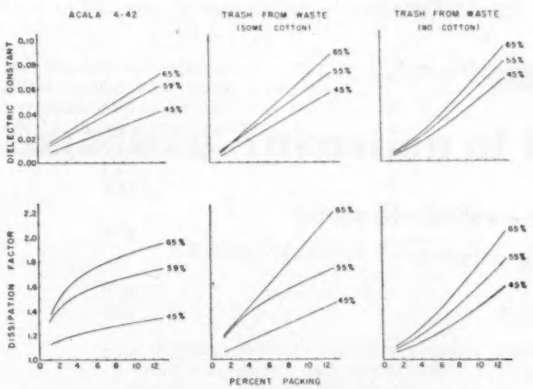

FIG. 5. *Effect of moisture (70°F, 200 kc./sec.).*

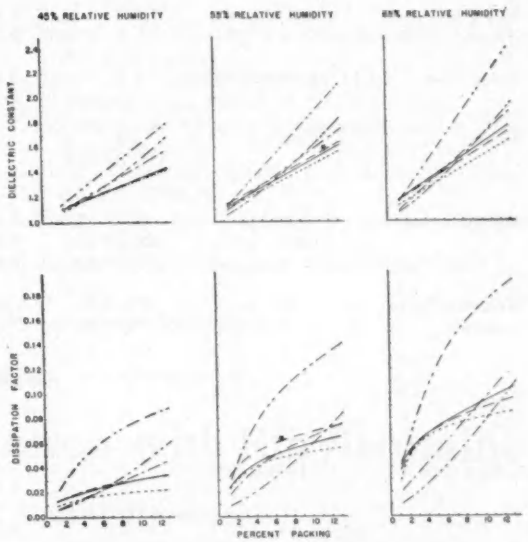

FIG. 6. *Comparison between three varieties of cotton and three varieties of trash at 45%, 55%, and 65% R.H. — — - -, trash with picker motes; — - -, trash from waste (no cotton); — -, trash from waste (some cotton); ———, "C"; — — —, Acala 4–42; - - - - - -, Pima (70°F, 200 kc./sec.). (Lower middle curve marked * was determined at 59% R.H.)*

TABLE II. EXTRAPOLATED DIELECTRIC CONSTANT AT DIFFERENT HUMIDITIES (70°F, 200 KC./SEC.)

	45% R.H.	55% R.H.	65% R.H.
Acala 4–42	3.93	5.26*	6.07
"C" cotton from New Mexico	4.05	5.24	6.41
Pima	3.80	4.92	5.51
Trash (with some cotton), #2 cleaner-section waste	5.49†	6.28	8.11†
Trash (with no cotton), #2 cleaner-section waste	6.92†	8.04†	9.20†
Trash, mill-mix picker motes	6.71	9.57	11.74

* 59% R.H.

† A straight line was assumed for all points above 20 g. in the condenser.

TABLE III. RESULTS FROM LITERATURE

	Frequency	Moisture (%)	Dielectric constant	Reference	Method
Cotton, transverse	1.755 mc./sec.	0	3.5	Balls [1]	$E_m - 1 = P(E - 1)$ with 24% packing
		5.4	6.0		
		6.2	6.7		
		7.5	8.0		
Cotton, axial	1.755 mc./sec.	0	6.0		
		5.4	11.4		
		6.2	12.6		
		7.5	14.9		
Nylon fiber	10 kc./sec.	0	4.2	Errera and Sack [3]	Immersion method
	500 kc./sec.	0	3.26		
Nylon film	11 kc./sec.	0	4.0	King [5]	
		4	8.0		
Nylon fiber	3,000 mc./sec.	2	3.13	Shaw and Windle [8]	Lichtenecker equation: $\log E_m = P \log E$
Nylon	1,000 c.p.s.	70 (18% R.H.)	4.0	*Textile World's* "Synthetic Fiber Table" [10]	
Molded nylon	60 c.p.s.	0% R.H.	3.2	Du Bois [2]	
	1,000 c.p.s.	50% R.H.	3.3		
	1 mc./sec.	0% R.H.	3.6		
Molded cellulose acetate	60 c.p.s.	50% R.H.	3.5–6.4	Du Bois [2]	
	1 mc./sec.	50% R.H.	3.2–6.2		
				Hearle [4]	Extrapolated straight line drawn between unity at 0% packing and the measured dielectric constant at the indicated packing factor:
Cotton yarn	100 kc./sec.	0	3.0		43.3
		5 (45% R.H.)	4.4		44.5
		6.5 (65% R.H.)	6.0		45.4
Nylon staple	100 kc./sec.	0	2.4		52.2
		3.5 (45% R.H.)	2.6		52.9
		4.5 (65% R.H.)	2.9		53.9
Nylon continuous filament	100 kc./sec.	4.5	3.2		87.0
Acetate staple	100 kc./sec.	0	2.5		44.4
		4 (45% R.H.)	2.9		45.4
		6 (65% R.H.)	3.3		47.1
Acetate continuous staple	100 kc./sec.	6	3.7		78.8

Conclusions

The variation of dielectric constant of the mixtures for packing factors above 12.9% cannot be determined except by making an assumption. Numerous relations have been proposed, but none seems to give satisfactory results. Hence, the extrapolated values for dielectric constant were based only on the data obtained, assuming no change in the curve above 12.9%.

TABLE IV. COMPARISON OF EXTRAPOLATED AND COMPUTED VALUES OF DIELECTRIC CONSTANT
(70°F, 55% R.H., 200 KC./SEC.)

	Nylon	Acetate rayon
Extrapolated value	2.79	3.14
$E_m - 1 = P(E - 1)$	2.77 ± .02*	3.17 ± .02*
Lorentz equation	4.65 ± .06*	7.69 ± .32*
Lichtenecker equation	4.95 ± .05*	7.33 ± .22*

* These values are averages for 10 different packing factors.

Increasing the moisture content of the cotton increased the values of the dielectric constant and dissipation factor. No calculations were made to determine if the increased value was due wholly to the added moisture.

The differences between the various mixtures of cotton and trash can be observed without making use of the extrapolated values. There appears to be very little difference in the dielectric constants of the rain-grown and irrigated varieties. The spread of dissipation factor follows that of the dielectric constant.

Using the extrapolated values at 45%, 55%, and 65% R.H. reveals the dielectric constant of trash with some cotton to be 32% more than that for cotton alone, trash with no cotton to be 62% more, and trash containing picker motes to be 84% more.

Tests of this type are useful in determining the electrical characteristics of cotton and trash. They might be of value in the determination of the trash content of cotton, and may lead to some method of separating the trash from the cotton.

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(*Manuscript received February 1, 1954.*)

Extensive Animation of Cotton with Ethylenimine

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Abstract

Aminated cottons of nitrogen contents ranging up to 29% are prepared by heating chemical cotton with ethylenimine at 140°–180°C. These products are considerably different from cellulose in their physical and chemical properties. A possible chemical structure for these materials is discussed but is shown to be not entirely satisfactory.

Introduction

In the course of studying chemical modifications of cellulose, the reaction of cotton and ethylenimine was investigated under conditions of moderate pressure, excess ethylenimine, and relatively high temperature. The prime concern of the considerable patent literature on the treatment of cellulose with ethylenimine appears to be the production of a slightly modified cellulose (of a low amino nitrogen content), in the hope of obtaining more desirable dyeing properties and a more durable fiber [1, 2, 3]. Gardner [4] found that ethylenimine would "react with the free hydroxyl groups of cellulose acetate" to produce materials containing 1% nitrogen. The reaction was formulated as

$$\text{cell—OH} + \underbrace{\text{CH}_2\text{—CH}_2\text{—NH}} \rightarrow \text{cell—O—CH}_2\text{CH}_2\text{NH}_2.$$

In a search for aminated cellulose of low nitrogen

content, Guthrie [5] obtained cotton fabrics of 0.6% amino nitrogen content through the use of 2-aminoethylsulfuric acid in strong caustic solution under moderate conditions of time and temperature. These materials dyed readily with acid wool dyes. In a continuation of this work [3] raw cotton fibers were heated with ethylenimine vapor at 100°–110°C, using an amount of imine equal to 4% of the weight of the cotton. The product contained 0.33% nitrogen (air-dry basis). After 6 hrs. of kier boil the nitrogen content was 0.12%. Recently, Drake and Guthrie [6] have reported the preparation of aminoethylated cellulose with nitrogen contents up to 5%.

The present paper discusses (*1*) experiments with ethylenimine and cotton which had as their goal the preparation of materials of much higher amino nitrogen content, (*2*) the physical and chemical characteristics of the products, and (*3*) their possible chemical nature.

Experimental

Materials and Apparatus

Chemical cotton (Chemical Cotton Co., Chattanooga, Tenn.) was soaked for 3 days in distilled water (Figure 1). The soaked linters were suspended in water and subjected to chopping in a high-speed knife-edged blender. After transferring to a Büchner funnel and further rinsing, the wet fibers were allowed to air-dry for several days and the resulting matted material was chopped (dry) in the blender. Ethylenimine, obtained from various commercial sources, was stored over potassium hydroxide pellets. Small quantities (200 ml.) of the material were distilled through a Vigreux column, and the fraction was collected in the range 55°–56°C employed in all experiments. The distilled imine was stored in the cold. (WARNING: Ethylenimine is toxic as well as very corrosive to skin and membrane. It should be handled with the greatest of care.)

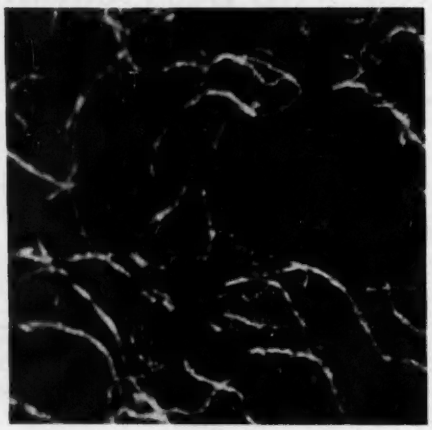

FIG. 1. *Chemical cotton.**

*The photographs were made on Super XX 35-mm. film with a Leica camera attached to one side of the lens system of an American Optical Stereomicroscope. Reflected illumination was used. (Magnification, 36 ×.)

The reactions were performed in a "super-pressure reaction vessel, micro series" (American Instrument Co., Silver Spring, Md.). The internal dimensions of the two metal bombs employed were $8\frac{1}{4}$ in. × $1\frac{1}{32}$ in. and $1\frac{1}{2}$ in. × $10\frac{1}{2}$ in. The apparatus was not equipped with a pressure gage. The temperature was monitored by means of a recording potentiometer. The durations of the reactions were timed automatically. The reaction mixtures were brought to operating temperatures within 20 min., and at the end of the run were permitted to cool to room temperature in about 1 hr.

TABLE I. AMINOETHYLATIONS

Run	Temp. (°C)	Time (hrs.)	Nitrogen (%)
38	140–150	4.5	2.65
31	140–145	4.5	3.25
4	150–170	4.5	4.0
35	160	4.5	4.3
93	175–180	1	9.5*
89	175–195	6	10.1†
65	135–150	6.5	12.4
52	175	5	14.1
54	155–175	3.5	18.3
76	175–195	6	15.7‡
91	175–195	6	20.5§
92	175–195	6	16.9‖
102	175–180	22	18.6
106	195	19	19.5
108	195	6	18.3¶
173	167	18	18.9
175	171	18	20.4

* In runs 92–108, inclusive, 10 ml. of imine was used.
† Cotton was dried over phosphorus pentoxide *in vacuo*.
‡ Three grams of cotton were used with 10 ml. of imine.
§ Five grams of dioctyl phthalate were added as a "plasticizer."
‖ Five grams of polypropylene glycol were added as a "plasticizer."
¶ Regenerated cellulose (xanthate process) was used.

Aminoethylation ("Low Nitrogen") *

Two grams of chemical cotton, 5 ml. of benzene (thiophene-free), and 1.5 ml. of ethylenimine (2.36 moles of imine per mole of anhydroglucose) were placed in the glass liner (100 ml.) of the $1\frac{1}{32}$ in. × $8\frac{1}{4}$ in. bomb and heated at 140°–145°C for 4–5 hrs. After removal from the liner, the contents were agitated in distilled water for 5 min. and the excess water was decanted. This washing cycle was repeated until the effluent was free of base (phenolphthalein paper). The wet fibers were pressed free of excess water, pulled apart, and permitted to air-dry for 24 hrs. Final drying was over phosporus pentoxide *in vacuo*. The yield of thoroughly dried material was 2.4–2.8 g. The materials analyzed from 4%–6% amino nitrogen (Kjeldahl analysis)—that is, approximately 0.5–0.9 aminoethyl group per anhydroglucose unit.

Because the emphasis in this work was on high-nitrogen products, the preparation of materials of lower nitrogen content—that is, up to 16%—was not completely explored. Sufficient experiments were performed, however, to indicate that any amine nitrogen content in this range could be obtained by suitable adjustments of reactant concentrations, temperature, and time. Some additional experiments are shown in Table I.

Physical behavior of "low-nitrogen" aminoethylcellulose.—The material was soft and resembled the original cotton closely. Under the microscope the fibers appeared to have undergone little change in length, but had increased in diameter (Figure 2). The wet fibers were silky and somewhat translucent, and tended to stick to glass and metal surfaces. The materials fluoresced a bright blue under the ultraviolet. Occasionally, the product had a light yellow color, possibly due to the presence of polyethylenimines, which are readily formed by metallic contaminants.

Aminoethylation ("High Nitrogen") *

Two grams (0.0123 mole) of air-dried cellulose and 20 ml. (0.386 mole) of ethylenimine were placed in the Pyrex liner of the $1\frac{1}{2}$ in. × $10\frac{1}{2}$ in. bomb. The materials were kneaded with a glass rod in order to saturate the cellulose with the reagent. The bomb was heated for 18 hrs. at 167° ± 2°C. After cooling, the contents were washed and dried in the same manner as for the low-nitrogen reactions. The yield of completely dried, somewhat brittle, material was 5.5 g. The amino nitrogen content (Kjeldahl) was 19%–20%. It is noteworthy that the fibers' increase in weight, 3.5 g., if simply attributed to some kind of addition of ethylenimine to cellulose, would yield a product of this nitrogen content.

*Although Gardner's formulation of the reaction between cellulose and ethylenimine is quite reasonable, it has not been definitely established as being correct. For purposes of this discussion, however, our reaction products are termed "aminoethylcelluloses," the process called "aminoethylation," and the reaction presumed to be the one given by Gardner.

The arbitrary designations of "low nitrogen" and "high nitrogen" refer to amino nitrogen contents of 2%–6% and 16%–29%, respectively.

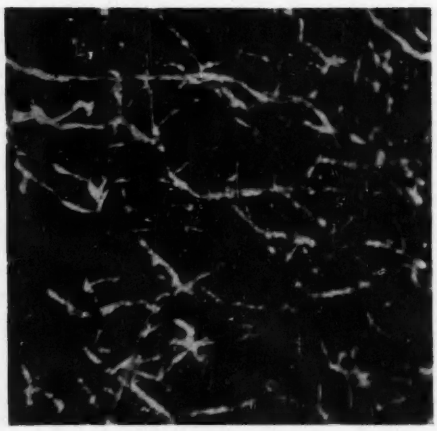

FIG. 2. *"Low-nitrogen" aminoethylcellulose (3% amino N).*

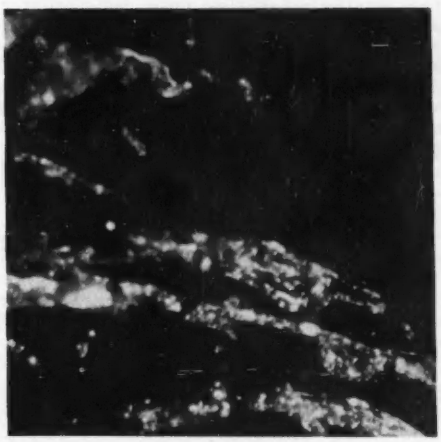

FIG. 3. *"High-nitrogen" aminoethylcellulose (21.1% amino N).*

Physical behavior of "high-nitrogen" aminoethylcellulose.—

(*a*) The wet fibers exhibited all the characteristics of the low-nitrogen products, but to a greater degree. Thus, they were highly swollen, quite translucent in suspension, and seemed to have considerable tensile strength (Figure 3).

(*b*) Products which had been washed and thoroughly dried, all without exposure to the atmosphere, remained soft. Upon exposure, however, there was a gain in weight and the materials became somewhat brittle.*

(*c*) Although a large number of organic solvents were tried individually and in various combinations, the materials proved insoluble. A considerable degree of solubility was exhibited, however, in cold 72% sulfuric acid.

(*d*) A number of experiments were performed on the effects of hot water and hot solvents on the products (Table II). It can be seen that losses in nitrogen content were relatively small.

Experimental Aminoethylations

Table I lists various experimental aminoethylation reactions. The first two runs were performed according to the low-nitrogen aminoethylation procedure, with temperature exceptions as noted. Runs 173 and 175 were high-nitrogen aminoethylations. This latter procedure was used in the remainder of the runs, with the modifications noted. Where temperature was not precisely controlled, the temperature ranges are given.

Reaminoethylation

Table III contains the results of reaminoethylation experiments—that is, the subjection of an aminoethylcellulose to repeated reactions with ethylemimine. The procedure was essentially the same as that for high-nitrogen aminoethylation. The best products, from the standpoint of yield, nitrogen content, and lack of color, were obtained by observing the following precautions: (*a*) using aminoethylcellulose which had not had excessive exposure to the atmosphere; (*b*) holding the temperature in the range 155°–160°C; (*c*) avoiding the presence of metallic impurities; (*d*) packing the charge loosely in the liner. A typical sequence of nitrogen contents from successive reactions is shown in Table III.

The properties of the reaminoethylated materials were those of high-nitrogen aminoethylcellulose, but accentuated. There was a decided shortening of fiber length (Figure 4).

Discussion

One can arrive at a possible structure for aminoethylcellulose by assuming that the initial phase of the reaction of cellulose and ethylenimine is an aminoethylation as given by Gardner [4]. To explain the much higher nitrogen contents obtained, it is assumed, as has been suggested by Drake and

* When the isolation of products is performed as described in the given aminoethylation procedures the materials obtained are, actually, not cellulose amines but cellulose amine carbonates. It was observed that carbonate formation could be prevented if, after the reaction, the product was washed and dried without undue exposure to the atmosphere. Further, decarbonated materials could be obtained from the carbonates by (1) simply boiling the latter in 1% sodium hydroxide for 3–4 hrs. or by (2) shaking the carbonates with 5% hydrochloric acid (by volume) for 24 hrs.

TABLE II. EFFECT OF SOLVENTS ON AMINOETHYLCELLULOSE

No.	Nitrogen (before) (%)	Treatment	Nitrogen (after) (%)
53	19.6	90 min. boiling water;	17.0
		additional 4 hrs. at 80°C	17.0
76	15.7	20 hrs. refluxing in 50/50 methanol-benzene	14.5
88	23.6	4 hrs. boiling water	21.7

TABLE III. REAMINOETHYLATION

Run	Nitrogen (before) (%)	Nitrogen (after) (%)	Comment
		First reaminoethylation	
88	15.7	23.6	2 g. AEC, 10 ml. imine
3–17	18.6	23.3	4.5 g. AEC, 10 ml. imine
107	14.9	22.6	4.1 g. AEC, 10 ml. imine
3–176	18.9	24.6	153°C
3–177	19.6	24.8	
3–178	20.4	24.4	155°C
		Second reaminoethylation	
179	24.6	26.2	
181	24.4	26.6	
		Third reaminoethylation	
183	26.2	27.8	
185	26.6	29.0	

Guthrie [6], that ethylenimine reacts further with the primary amino groups of the aminoethyl ether to form polyethylenimine chains, such as

$$\text{cell—[O(CH}_2\text{CH}_2\text{NH)}_x\text{CH}_2\text{CH}_2\text{NH}_2]_3,$$

where x is some small integer (1, 2, 3, etc.).*

In support of such a structure, the following information can be given:

(*1*) If an ethylcellulose ether (degree of substitution, 2.6) is subjected to aminoethylation, the recovered product is essentially unchanged ethylcellulose with a very small nitrogen content (0.3%). This would appear to indicate that, in some way, the successful aminoethylation of cellulose requires the presence of hydroxyl groups.

(*2*) If a mixed acid nitration of a high-nitrogen aminoethylcellulose is attempted, one obtains a product which, in its physical and chemical properties, is unlike nitrocellulose, and, moreover, is unstable. The material, difficultly soluble in H_2SO_4 and not a nitrate ester, is perhaps a nitramine.

(*3*) It is well known that cellulose dissolves readily in cuprammonium solution, and it is believed that dissolution results from the interaction of the hydroxyl groups of cellulose with the cuprammonium cation [7]. In qualitative experiments it was observed that a low-nitrogen aminoethylcellulose (3.9% N) was only partially soluble in cuprammonium solution, and a high-nitrogen sample (18.2% N) was quite insoluble. Cellulose, under the identical procedure, gelled at once and dissolved completely in 15 min. The results in Table IV were obtained with aminoethylcelluloses which were shaken in cuprammonium solution for 45 min. at room temperature. In order to remove all the copper, the samples were soaked in 15% hydrochloric acid overnight and washed successively with water, concentrated ammonia, water, and alcohol. The materials were dried over phosphorus pentoxide.

From the fact that high-nitrogen aminoethylcelluloses are quite insoluble it is concluded that there are few, if any, free hydroxyl groups available for complexing with cuprammonium cations. On the other hand, it would seem that in low-nitrogen materials a large percentage of the hydroxyl groups must remain undisturbed. This belief is supported by the ready nitration of such materials (4%–6% N) to yield aminoethylcellulose nitrates (10%–11% nitrate nitrogen) (Figure 5). A photograph of nitrocellulose is included for purposes of comparison (Figure 6). These latter products proved quite insoluble, which is surprising considering the ready solubility of 10–14% nitrate nitrogen nitrocellulose. This observation, coupled with the considerable insolubility of low-nitrogen aminoethylcelluloses in cuprammonium solution shown in Table IV, strongly suggests that the formulation of aminoethylcellulose as, essentially, an aminoethyl ether is not strictly correct, and is probably an oversimplification. Other changes have occurred in the cellulose molecule, and it is these which are primarily responsible for the insolubility of the material.*

*For leading references and a discussion of the polymerization of ethylenimine, see G. D. Jones *et al., J. Org. Chem.* **9**, 125 (1944).

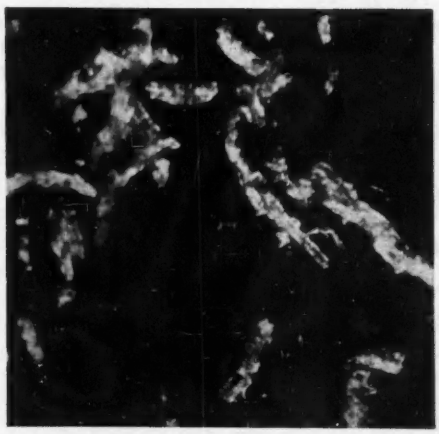

FIG. 4. *"High-nitrogen" aminoethylcellulose (reaminated) (23.2% amino N).*

* The extreme insolubility of these aminoethylcelluloses suggests the possibility of cross linking, but it is difficult to explain how this would occur. A reviewer has suggested that branched polymers are possible. These may well contribute to the insolubility of high-nitrogen aminoethylcellulose, but do not, in any way, explain the insolubility of highly nitrated, low-nitrogen aminoethylcellulose.

TABLE IV. ACTION OF CUPRAMMONIUM SOLUTION ON AMINOETHYLCELLULOSES

Sample	Nitrogen (%)	Recovery (%)	Final nitrogen (%)
44	1.85	74	1.65
3–120A	9.0	82	9.3
3–57	11.4	91	11.6
3–120B	14.6	84	13.9
3–74	18.2	87	19.2

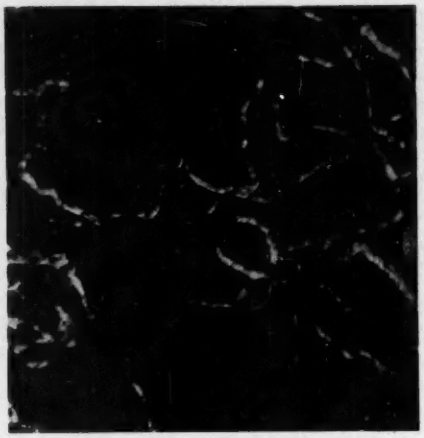

FIG. 5. *"Low-nitrogen" aminoethylcellulose nitrate (11.2% nitrate N).*

(*4*) Undoubtedly the most serious deterrent to the aminoethyl ether hypothesis is the fact that no report exists in the literature on the unquestionable aminoethylation of a relatively simple alcohol with ethylenimine. In this laboratory a number of attempts with simple aliphatic alcohols, both liquid and solid, under a variety of conditions of time, temperature, concentration, and catalyst have failed to yield a positively identifiable β-aminoethyl ether. In most cases the alcohol was recovered in excellent yield. Equally unsuccessful were the experiments with 1,10-dihydroxydecane, inositol, and pentaerythritol. On the other hand, both polyvinyl alcohol and starch appear to react with ethylenimine.

Acknowledgment

The authors are indebted to Messrs. Edward N. Gerhardt and Robert P. May for the performance of analyses and nitrations, to Messrs. Eugene R. Weiner and Bertram Grollman for the photographs, and to Dr. Dirk Reuyl for the translation of Dutch technical literature.

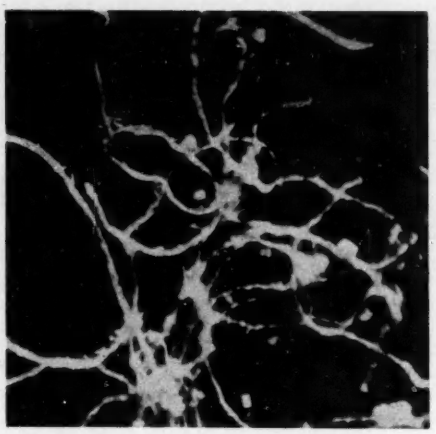

FIG. 6. *Nitrocellulose (13.1% nitrate N).*

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(*Manuscript received April 13, 1954.*)

STRESS—STRAIN BEHAVIOR

A Symposium

The Textile Division of the Massachusetts Institute of Technology, Mechanical Engineering Department, is sponsoring a two-day Symposium on Stress-Strain Behavior October 6 and 7, 1954, at Cambridge, Mass.

The topics covered in the Symposium will not be confined to the subject of filamentous high polymers but will include a range of other material solids. It is hoped that such a diversified program will facilitate exchange of ideas among scientists and engineers whose work is supported by different industries.

Specifically, the Symposium will deal with (1) recent developments in the techniques for obtaining stress strain data and (2) advances in the interpretation and use of such data. The program for the second day deals principally with subjects directly within the sphere of textile interest.

For further information, contact Prof. Stanley Backer, Mechanical Engineering Department, Massachusetts Institute of Technology, Cambridge, Mass.

Measurement of Triboelectric Response of Raw Cottons*

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Abstract

By use of a novel commutator method, triboelectric potentials produced by rubbing cotton with various materials have been measured by comparison with known D.C. potentials. Results are given here for fiberboard (phenolic resin laminate, fabric base), cork roller material, synthetic rubber roller material, Lucite, polystyrene, glass, and cellulose acetate sheet, used as rubbing materials on three varieties of cotton and trash extracted from baled cotton. The purpose of this study was to learn if the sufficiently great differences in triboelectricity produced by cottons and trash could be used practically in the electrostatic cleaning of cotton.

IT was thought that since so much electric charge can be produced by fiber contact and friction with various materials, a study should be made of these triboelectric effects to determine if purposely generated triboelectric potentials can be used to practical advantage in a cotton cleaning machine.

Methods

One method of measuring triboelectric charges employs a Faraday ice-pail technique, in which the cotton sample is placed on an insulated support inside a metal container which is also well insulated and connected to an electrometer. Any charge generated on the cotton (by rubbing it with different materials) induces an opposite charge on the inside of the container, repelling a like charge to the electrometer. The electrometer was calibrated to measure volts, so that the charge produced on the cotton could be computed by multiplying the voltage by the capacity across the electrometer.

This method gives results that vary considerably with the manner of rubbing the sample. Both velocity and pressure of rubbing changes the magnitude of the results, and for some rubbing materials may even reverse the sign of the charge.

A mechanical method of rubbing the sample always with the same velocity and pressure was developed, in which the rubbing material is held in contact with the cotton by a light spring and rapidly jerked over the cotton by the triggered release of a stretched spring (see Figure 1). Usually 50 readings were taken with each sample.

Some cotton duck was used in place of the cotton fibers to check the reproducibility of measurements on different days; the spread between the average values was less than twice the average standard error of any one set of readings. Values of charge and

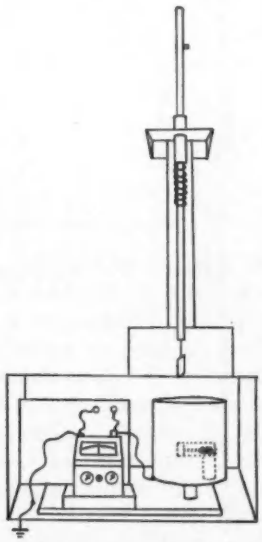

FIG. 1. *Ice-pail method.*

* A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract is being supervised by the Southern Utilization Research Branch of the Agricultural Research Service.

TABLE I. ELECTROSTATIC CHARGE ($\mu\mu C$)

R.H. (%)	Fiberboard Charge	Fiberboard Std. error	Leather Charge	Leather Std. error	Lead Charge	Lead Std. error	Lucite Charge	Lucite Std. error	Masonite Charge	Masonite Std. error	Polystyrene Charge	Polystyrene Std. error	Rubber Charge	Rubber Std. error
							Acala 4–42							
65	37	1			12	0.4					531			
	54	1			15	0.5					432	16		
	37	1												
	233	9												
45	240	12	665	25			−275	15	144	20	510	11	315	26
	270	9					−305	8	147	31			350	29
	245	14					−315	6	173	13			315	23
	350	25							180	9				
	390	8							101	5				
	456	15												
	402	10												
	544	22												
	183	5												
	274	5												
							"C"							
65	539	20												
	699	7												
	483	11												
	725	19												
	191	12												
45	285	15							165	5			350	39
	245	11											350	14
	455	21											385	19
	282	9												
	227	3												
							DPL							
65	30	0.9			21	0.7								
	168	5												
	31	0.9												
	37	1												
	191	8												
45	497	12												
	532	12												
	235	12												
	478	21												
							Duck Cloth							
65	34	0.7			9	0.4	Inconsistent				490	13		
	159	3									257	7		
	33	0.7												
	34	0.8												
45	193	5												
	201	4												
	200	5												
	194	9												
	206	5												
	193	6												
	317	18												
							Mesilla Valley							
65	195	10												
	142	16												

TABLE I—*Continued*

R.H. (%)	Fiberboard Charge	Fiberboard Std. error	Leather Charge	Leather Std. error	Lead Charge	Lead Std. error	Lucite Charge	Lucite Std. error	Masonite Charge	Masonite Std. error	Polystyrene Charge	Polystyrene Std. error	Rubber Charge	Rubber Std. error
							Picker Motes							
65	254	9					− 12	0.3			389	18		
	180	6					− 13	0.6			342	14		
	194	9									659	14		
											575	24		
45	375	9												
	463	14												
							Pima							
65	210	9					Inconsistent							
	277	4									734	24		
	176	7									738	21		
	238	16												
45	150	6					−200	10	90	4	385	28	490	29
	210	14							175	25	675	27	315	32
	240	4							175	16			245	47
	350	6												
	280	10												
	296	9												
	281	4												
	312	9												
	483	19												
	458	15												
	311	19												
							Trash (with cotton)							
65	60	2			17	0.4	− 32	3			636	36		
	128	8			18	0.6	−105	4			647	36		
											447	19		
45	484	11												
	476	7												
							Trash (with no cotton)							
65	12	0.3					Inconsistent				24	1		
	14	0.2									38	1		
	22	1.6									656	25		
											430	18		
45	20	0.4												

standard error produced on the several cottons and trash samples are shown in Table I.

A second method of measuring triboelectricity, similar to that used by Hayek and Chromey [6] of du Pont (see Figure 2), was used to measure the charge on cottons and trash. The sample is mounted on a polystyrene insulator on one side of a rotatable cylinder so that by rotation of the cylinder the sample passes under the rubbing material; farther around the circle it moves near a small pickup plate connected to the grid of a vacuum tube. The output of this tube is amplified and displayed on a cathode-ray oscilloscope and also on a high-speed recorder. On the side of the cylinder diametrically opposite to the cotton sample an identical insulated plate is similarily mounted so that it can be given a charge from a known variable potential when it is even with the rubbing material. Farther on, this plate gives the grid of the vacuum tube a pulse similar to the one given by the rubbed cotton. The cotton support is staggered on the cylinder axially with the calibrating conductor so that the cotton cannot be touched

by the charging wire and the calibrating plate cannot be touched by the rubbing material. Thus, alternate pulses on the scope are given by the charged cotton and the others by the comparison potential. The comparison potential is varied by a Variac on the primary supply until it gives pulses the same size as those given by the charged cotton sample, as shown in Figure 3. The cylinder has a diameter of 6.5 in. and revolves at a rate of 485 r.p.m.

Discussion of Results

The ice-pail method showed no consistent difference between the cottons. Trash usually gave lower charges than cotton, although there were some exceptions for certain rubbing materials. Metals on cotton gave very small charges, which changed with the degree of polish of the metal. In some cases there was a polarity change between the polished and unpolished metal, and in other cases there were random polarity changes. Unpolished aluminum gave a positive charge to the cotton, while polished aluminum gave a negative charge. Several metals —galvanized iron, tin, aluminum, copper, lead, duraluminum, and steel—were tested at 45% R.H. Galvanized iron, tin, copper, and steel gave consistent positive charges to the cotton, lead gave a negative charge, and aluminum and duraluminum gave both positive and negative charges. At 65% R.H. lead gave a positive charge to the cotton, while the other metals gave results too small to observe. No consistent data could be obtained by rubbing cotton on cotton. Lucite gave both positive and negative charges to the cotton. Table I is incomplete because the ice-pail method was discontinued in favor of the commutator method, which seemed more consistent and reliable.

For the commutator method the repeatability and consistency of the readings were good when run at any one time and often good for different times, although occasionally repeats at different times gave large variations. A tremendous amount of study on both methods failed to show the reasons for the isolated cases of inconsistency that occurred under seemingly identical conditions. It is believed that this experience is more or less common to most researchers in this field. The average deviation for repeated tests at different times was 22%. Part of the deviation was due to the fact that the repeated tests were made at a slightly different relative humidity.

Differences in pressure of the rubbing material on the cotton may cause variations in the potential. Table II shows these variations for several rubbing materials on a limited number of samples. A resistance strain gage was mounted on the arm supporting the rubbing element to set the pressure the same value for all samples. The pressure was more critical for the softer rubbing materials.

The slightest contamination of the samples causes variations in the results, and continued use of some rubbing materials alters the results. In order to eliminate these difficulties, a large number of fresh samples were made with the greatest care. Ten samples of the three varieties of cotton and trash were used for each test. The fibers were carefully paralleled and wrapped over the face of a clean block

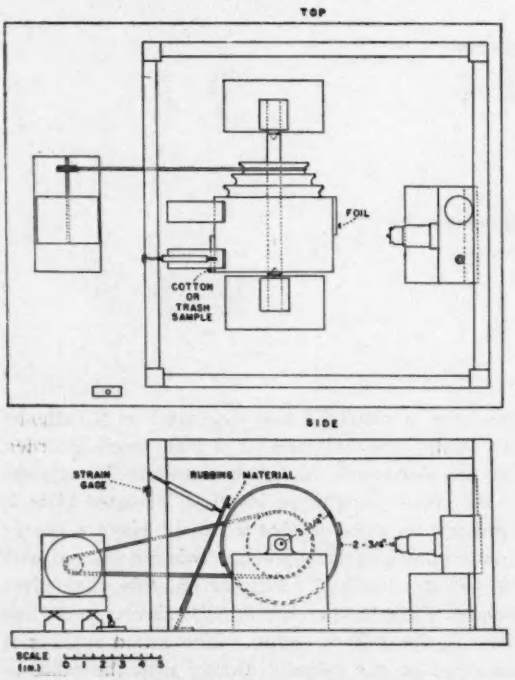

FIG. 2. *Rotating-cyclinder comparison method for measuring triboelectric charges.*

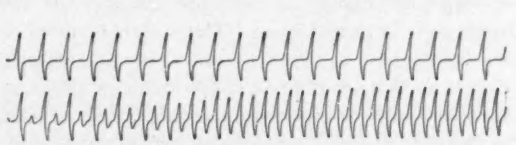

FIG. 3. Top—*Pulses from cotton alone.* Bottom—*Alternate calibration pulses added.*

of Lucite $\frac{3}{8}$ in. × 2 in. × $\frac{1}{16}$ in., and the ends of the fibers were glued on the back of the block, which in turn was cemented to a polystyrene block $\frac{1}{4}$ in. thick. This block was curved to fit the cylinder and was mounted on the cylinder by means of a screw fixed in the back of the polystyrene block. The fibers were completely insulated from the metal cylinder, which was grounded. A similar combination block covered with tin foil was used to carry the charges produced by the known potential.

The voltages produced by rubbing cotton with cork, fiberboard, Lucite, glass, and cellulose acetate were essentially constant after 1-min. running time. There were cases in which there was a slight increase with running time, and others in which there was a slight decrease. A later recheck was made at 65% R.H. by rubbing cellulose acetate on Acala 4–42 and DPL 15. These rechecks gave negative voltages at about the same magnitude as those generated with Pima. There were occasional polarity changes with Lucite. The voltage generated by rubbing cotton with polystyrene was essentially constant after 1 min. at 65% R.H., but at 45% R.H. the voltage usually built up to a high positive value and then decreased. In several cases, when the surface of the rubbing material became scratched, the voltage decreased to zero. When glass was used, the generated voltage increased to the full value almost instantly. The voltage generated by cork usually built up gradually during the first few minutes (Table III).

The tribovoltages generated on cotton varied from over 6,000 v. positive with fiber board to over 7,000 v. negative with sheet cellulose acetate. The voltages generated by the fiberboard were the most consistent of all the rubbing materials. The average coefficient of variation was 6.11% for the eight runs, and the average deviation was 7.08% for the seven repeated checks on different days.

The voltages generated by the plastic materials were greatly affected by the surface condition of the rubbing material. The more finely polished surfaces gave the higher voltages. The voltages generated by cork varied somewhat, but were the least affected by the roughness of the surface.

There was a consistent increase in voltage with running time using synthetic roller material on cotton. In some instances the voltage built up to a high negative value during the first minute, and then changed to positive during the running time. No consistent results could be obtained using a composition roller material; there was a continuous increase in the positive direction.

Positive voltages were generated at 65% R.H. on the cotton by Bakelite, shellac, a Georgia talc, micarta, and red roller varnish. Unpolished Bakelite

TABLE II. EFFECT OF PRESSURE ON GENERATED VOLTAGE

Rubbing material	Cotton or trash	R.H. (%)	Generated voltage pressure 1*	pressure 2*	pressure 3*	Average voltage	Std. deviation	Std. error	Coeff. of variation (%)
Cork	Acala 4–42	63	1109	1192	1522				
		63.5	1593	1682	1838				
	Pima	67	1463	1829	2006				
		63.5	1186	1339	1699				
	Trash	65.5	614	661	1133				
Lucite	Pima	62	496	472	437	468	30	21	6.41
Polystyrene	Acala 4–42	67	1180	1121	1145	1149	24	17	2.09
		66	1151	1239	1316	1235	67	47	5.43
	DPL 15	66	1210	1245	1469	1308	115	81	8.79
		63	1475	1463	1339	1426	32	22	2.24
	Pima	65	1239	1056	1192	1162	94	66	8.09
Glass	Acala 4–42	63	−1540	−1505	−1505	−1517	16	11	1.06
	Pima	68.5	−1198	−1434	−1493	−1375	127	90	9.24

* Pressure 2 was approximately twice pressure 1, and pressure 3 was three times pressure 1.

TABLE III. ELECTROSTATIC VOLTAGE

Rubbing material	Cotton or trash	R.H. (%)	Generated voltage	Std. deviation	Std. error	Coeff. of variation (%)
Fiberboard	Acala 4–42	65	2396	217	72	9.06
		60	3366	325	108	9.66
		45	5788	337	112	5.82
	DPL 15	66	2840	166	63	5.85
		60	4469	194	112	4.34
		45	6057	267	94	4.41
	Pima	66	1857	121	43	6.52
		45	5900	189	77	3.20
	Trash	68	1093	241	85	22.05
		42	1415	641	214	45.30
Cork roller	Acala 4–42	63	1320	270	95	20.45
		54	2167	304	107	14.03
		44	4462	296	112	6.63
	DPL 15	68.5	1808	145	51	8.02
		46	4369	615	205	14.08
	Pima	63.5	1547	210	70	13.57
		46	4402	269	95	6.11
	Trash	65.5	613	217	72	35.40
		46	1575	473	167	30.03
Synthetic rubber	Acala 4–42	65	930	144	51	15.48
		45	6011	869	328	14.46
	DPL 15	65	1339	147	60	10.98
		44	4437	627	209	14.13
	Pima	65	577	206	69	35.70
		44	2586	953	318	36.85
	Trash	65.5	1025	446	149	43.51
		46	2963	644	228	21.73
Lucite	Acala 4–42	63	−1168	88	33	7.53
		47	−1718	523	185	30.44
	DPL 15	65.5	−1023	157	52	15.35
		50	−2360	324	115	13.73
	Pima	63	− 795	207	73	26.04
		50	−3805	774	254	20.34
	Trash	62	− 841	283	100	33.65
		47	90	25	13	27.78
Polystyrene	Acala 4–42	67	1073	288	102	26.84
		42	2295	763	254	33.25
	DPL 15	67	1147	176	59	15.34
		46	1564	1171	390	74.87
	Pima	66	747	298	99	39.89
		42	4106	2238	746	54.51
	Trash	65	− 10	136	48	
		46	− 291	198	66	68.04

TABLE III—*Continued*

Rubbing material	Cotton or trash	R.H. (%)	Generated voltage	Std. deviation	Std. error	Coeff. of variation (%)
Glass	Acala 4–42	63.5	−1485	87	29	5.86
		46	−3994	1019	340	25.52
	DPL 15	65	−1641	297	99	18.10
		46	−4873	726	242	14.90
	Pima	64.5	−1914	129	46	6.74
		46	−6438	531	188	8.25
	Trash	64.5	− 910	274	91	30.11
		46	− 243	165	83	67.90
Cellulose acetate	Acala 4–42	66	556	85	28	15.29
		41	−5682	665	222	11.70
	DPL 15	70	667	136	45	20.39
		68	561	223	79	39.75
		46	−7056	729	243	10.33
	Pima	67.5	−2047	262	87	12.80
		46	−7159	837	296	11.69
	Trash	70	− 180	106	53	58.89
		44	− 260	108	48	41.54

first generated a negative voltage on the cotton, and then changed to positive as the Bakelite became more polished. A negative voltage was generated on the cotton by mica, Fiberglas, and leather roller material. Shellac, a Georgia talc, red roller material, mica, and leather contaminated the cotton samples after a few minutes running time.

Three metals were tried; tin gave a positive charge to the cotton, and aluminum and copper gave a negative charge. The values were too small to obtain any accurate voltage measurements.

The voltage generated on trash for most rubbing materials was lower than that for cotton. A change in polarity was the rule, rather than the exception. Due to the rough nature of the trash, the surface of the rubbing materials became scratched, thus affecting the results considerably.

In general, the generated potentials for all the cottons and trash decrease with higher relative humidity, as shown in Table III and Figure 4.

Conclusions

A great number of factors affect the value of the voltage generated on cotton or trash by rubbing with various materials. It is difficult to draw definite conclusions as to the actual amount generated, but for most rubbing materials a great deal more voltage is produced on cotton than on trash.

The plastic rubbing materials tried would not be of any practical value for generating charges on cotton since the surfaces are easily scratched or roughened by any trash present. Fiberboard (phenolic resin laminate, fabric base) and cork roller material give consistent results and produce a relatively large tribovoltage difference for cotton and trash. Since these materials seem to be the least affected by the surface condition, they are the most practical for generating charges on cotton containing trash.

It does not seem that triboelectric methods can be used to distinguish between the various varieties of cotton, since the generated voltages are so nearly the same. But since there is a considerable difference between the voltage generated on cottons and on trash by some rubbing materials, it seems that practical use may be made of triboelectric methods to separate the trash from cottons.

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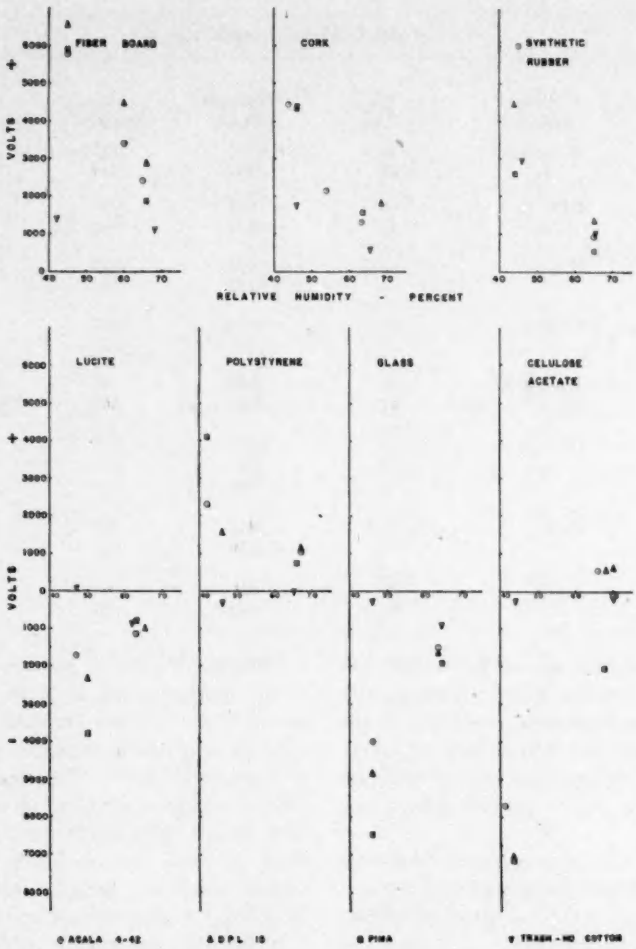

FIG. 4. *Triboelectric potentials for various cottons and rubbing materials.*

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(*Manuscript received February 26, 1954.*)

Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

On the Preparation of Cellulose *III* with Ethylamine

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New Orleans, La.
March 11, 1954

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Mann and Marrinan [1] reported that when bacterial cellulose is treated with anhydrous ethylamine, the manner in which the amine is removed affects the cellulose in different ways. Thus, if the amine is removed directly by evaporation, only a reduction in the crystallinity of the cellulose is observed, but no change in lattice type. However, if the amine is extracted with chloroform before appreciable evaporation can take place, cellulose *III* is produced. Large percentage conversion to cellulose *III* was claimed under the latter conditions. The presence of cellulose *III* was detected by infrared and x-ray diffraction observations. These workers state, "Since Conrad and co-workers [2, 3] using x-rays found no change in the type of crystal lattice, it is presumed that the ethylamine had evaporated off before the sample was placed in chloroform."

In our earlier work [2] the amine was quickly pressed out and the amine-wet cotton immersed in chloroform in open beakers to extract some of the amine which could not be pressed out. This was poured off and followed by extraction of the cotton with fresh chloroform in a Soxhlet apparatus containing phosphoric acid in the boiling flask. The preliminary extraction prevented a violent reaction with the phosphoric acid when the amine-rich solvent first syphoned over into the boiling flask. No appreciable evaporation of amine could have occurred in this case.

In our later work [3] a closed system was used. The amine was displaced by nitrogen under pressure; then, by application of just enough vacuum, the chloroform was drawn in directly onto the amine-wet cotton. Only after several washes with chloroform was the system opened and the sample transferred to a Soxhlet apparatus. Thus, less opportunity for evaporation of ethylamine was presented here than in the first case. In either case, the washed samples were extensively extracted with chloroform after the initial washings.

A later paper [4] describing our work with cotton cellulose and ethylamine shows that evaporation of ethylamine from amine-saturated cotton cellulose, either at atmospheric or under reduced pressure, converts the cellulose crystal lattice from cellulose *I* to cellulose *III*. This is at variance with the findings reported by Mann and Marrinan that only reduction of crystallinity occurs. We are reluctant to attribute this great difference in behavior merely to the difference in the source of the cellulose, even though we have reported that cotton cellulose *III* and ramie cellulose *III* behave differently toward boiling water.

The short communication of Mann and Marrinan only briefly described their experimental conditions, but enough information was given to permit a comparison of their conditions with ours. Our experiences suggest that the difference in results probably arises from the following factors.

First, we found that cellulose must be immersed for at least 4 hrs. for the lattice shift to occur on subsequent evaporation. Immersion of cotton cellulose for 1 hr. before evaporation did not shift the lattice; only reduced crystallinity resulted. This result is similar to the observation of Mann and Marrinan on bacterial cellulose immersed only 30 min. prior to evaporation of the amine.

Second, some recent unpublished work conducted in a pilot plant operation showed that incomplete removal of amine by washing with a solvent results in the formation of some cellulose *III* during or after drying of the washed cotton. We believe that this partial transformation is caused by a delayed evaporation of the residual amine in the cellulose. Thorough extraction of the treated cellulose with fresh solvent, such as we have achieved with a Soxhlet apparatus [2], is believed to be necessary in order to remove adequately the amine and avoid lattice shifts. If the bacterial cellulose treated by Mann and Marrinan was not thoroughly extracted with chloroform, then the appearance of the cellulose *III* lattice is not surprising.

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LEON SEGAL

The Influence of Repeated Torsional Deformations on the Birefringence of Nylon Monofilaments

CENTRAL LABORATORY T.N.O.
Delft, Holland
June 8, 1954

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Torsional fatigue experiments on monofilaments, carried out in our laboratories, were combined with an investigation on the birefringence of the fiber before and after the fatigue test. The preliminary experiments reported herein were performed on 3-den. nylon monofilaments.

In the original state the birefringence showed small differences along the fiber, the specific birefringence, Δ, in the greater part of the fiber being approximately 60, some smaller parts showing values of about 57. After the fatigue test again $\Delta = 60$ was most frequently found, but now the minimum values measured were considerably lower—*viz.*, approximately 30.

These results suggested that the effect of the fatigue action dominated in the parts which had originally a specific birefringence somewhat lower than the mean value. In order to establish this suggestion an apparatus was made in which the optical properties could be studied during the fatigue experiment on nylon filaments of 1 mm. length. Indeed it was found that Δ remained unchanged in the major part of the fiber while Δ in the part slightly less birefringent showed a sharp decrease during fatigue.

In this way it proved possible to predict the potential breaking points of a fiber from its optical properties.

Taking into account the above results one seems justified to assume that the destructive action of the repeated torsional deformation is accumulated in the places which originally possess a (slightly) lower degree of orientation than has the rest of the filament.

Our experiments are being continued and a detailed report will be published at a later date.

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J. ISINGS